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STABLE WHITE COATINGS

Report No. ARF 3207-5
(Interim Report)

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for

Jet Propulsion Laboratory
Pasadena, California

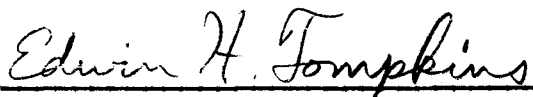Copy No. 61

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FOREWORD

This is Report No. ARF 3207-5 (Interim Report) of ARF Project C207. Contract No. 950111, (Subcontract under NASA Contract NASw-6), entitled "Stable White Coatings." The report covers the period from September 22, 1961, to April 1, 1962.

Personnel who contributed to this project include Dr. Caroline D. Miller (radiation effects and solar simulator design), Richard J. Larson (space chamber operation), O. Harry Olson (reflectivity and emissivity measurements), Yoshiro Harada and Harold L. Rechter (inorganic formulations), Dr. Nicodemus E. Boyer (organic coatings and synthesis), William K. Sumida and John Brzuskiewicz (organic preparations), and recently Gene A. Zerlaut in several areas. Major contributors to this report were C. Miller, Y. Harada, N. Boyer, H. Rechter, and G. Zerlaut.

Data are recorded in ARF Logbooks C 9164, C 11712, and C 11934.

Respectfully submitted,

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ABSTRACT

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A wide range of organic and inorganic coatings, vehicles and pigments have been exposed in a vacuum at about 10^{-6} mm to simulated solar radiation for periods equivalent to from 75 to 270 sun-hours. The general objective has been to develop stable coatings of high reflectivity and infrared emissivity suitable for long-range satellites. Spectral reflectivities determined before and after exposure show that ZnO and ZnS are unusually stable pigments, and that these pigments with pure potassium silicate and special silicone vehicles form the best coatings. Improved techniques of applying these materials to metal surfaces are being worked out.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

STABLE WHITE COATINGS

I. INTRODUCTION

This is the first interim report under the subject contract for the Jet Propulsion Laboratory. The period covered is from September 22, 1961, to April 1, 1962.

The basic objective of this program is to develop a white spacecraft coating of unusually high stability in solar radiation which can be applied by spraying or some other relatively simple technique to aluminum alloys or other materials used in the construction of long-range satellites and spacecrafts. The maximum temperature of application is not to exceed 300°F and the coating is to be adherent through temperature changes of 50°F/min. between 200°F and — 100°F. Stability in solar radiation is the prime requirement, but ratios of absorptivity to emissivity for solar radiation at 300°K to 350°K are to be in the range of 0.1 to 0.4. In other words, materials which absorb all the ultraviolet of space solar radiation, or which have some visible color, can be used if they have high stability. Since very few materials have the potential stability required for long-range probes in space, we have initiated work on some rather unusual coating formulations and we have spent a minimum effort on materials, such as many conventional organics, which deteriorate rapidly in intense UV. However, the effects of impurities (including water) are so pronounced in many pigments and vehicles that elimination of specific materials is not easy, and we are trying to sort out the various effects before designating a material as unusable. Just a preliminary analysis of photolysis in ZnO, which is included in this report, shows that the mechanism is quite complex, and that there are possible ways of upgrading a pigment considerably.

The work has been divided broadly into organic and inorganic. Organics provide better adhesion and other mechanical properties; some inorganics have outstanding UV stability. In order to reduce the complexity of the problems involved, a number of vehicles and pigments were exposed individually to simulated solar radiation. Changes in the spectral reflectivity curves are plotted for the more interesting materials and coatings.

We do not believe that simulated solar exposure is as routine as sometimes assumed, and we, along with other laboratories, are in the process of improving our techniques. With improved thermocouples, better trapping of pump oils, and more accurate measures of surface temperatures during exposure, we will have a more precise test for the special coatings which are being formulated on the basis of the results discussed in this report. For the comparative screening tests we have done so far, a precise solar intensity has not been essential.

In this field the divergent results obtained by different workers is somewhat disconcerting at times, and closer inspection of the problems involved in solar simulation and more thorough analysis of the mechanisms of photolysis in solids makes one much more cautious and less quick to

arrive at conclusions. However, one point does emerge from the increasing volume of information, and that is that much more stable coatings are a real possibility in the near future. Even some organics, normally considered to be unstable in UV, may be considerably improved by purification or modification, as discussed in subsequent sections of this report. Some of the recent reports from the Naval Research Laboratory are extremely interesting in this connection.

II. DESIGN OF SOLAR SIMULATOR

Any simulated environment, especially if designed to accelerate an environmental reaction, is of necessity an inexact recreation of the true conditions. However, these "true conditions" can be analyzed, and some rational approximation to the essential features can be designed, with reasonable expectation that materials exposed to these laboratory conditions will exhibit the same phenomena they would under actual use.

It is generally agreed that the conditions in space which most affect the performance of a highly reflecting white coating are solar radiation and vacuum. The solar spectrum, compiled by L. Jaffe, of the Jet Propulsion Laboratory, is given in Figure 1. (Also shown in Figure 1 is the energy spectrum of a typical AH-6 lamp at comparable total intensity.) The wavelengths below 2000 Å contribute less than 0.1% of the total energy and so may be disregarded without great error. Wavelengths above 4000 Å may be disregarded because they are not sufficiently energetic to break bonds, although approximately 90% of the energy is found at these longer wavelengths, and the total suitability of a coating for passive temperature control depends upon its high reflectivity in the visible region of the spectrum. On the basis of these considerations, the AH-6 lamp, a quartz-jacketed water cooled high pressure mercury arc, has been selected as the source of ultraviolet radiation.

The vacuum of the space environment is variously quoted at 10^{-9} to 10^{-15} mm Hg but the attainment of such pressures in the laboratory is time-consuming and probably unnecessary for the purposes of this work. At much higher pressures (10^{-6} mm Hg) there is no evidence of oxidative degradation, and the mean free path of evolved molecules is large compared to the dimensions of the chamber, so that further reduction in pressure would not be expected to change the results of the space simulation tests.

These principles guided the design of our space simulation chamber shown in Figure 2. It consists of a cylindrical chamber 24 inches in diameter, and 24 inches high, cooled by refrigerant coils on its outer surface, and capped with a torispherical head in which are mounted 3 AH-6 lamps. The distance from the lamps to the samples, mounted on a turntable beneath, can be adjusted to achieve variation of radiation intensity. The constancy of the radiation is monitored by reflecting a portion from a first surface mirror, mounted over the center of the turntable, through a quartz windowed viewing port on the head. The absolute intensity is measured before and after the run, using a wide-angle, temperature compensated thermopile. The spectral distribution of the radiation is measured with a Jarrell Ash Seya Namioka grating monochromator.
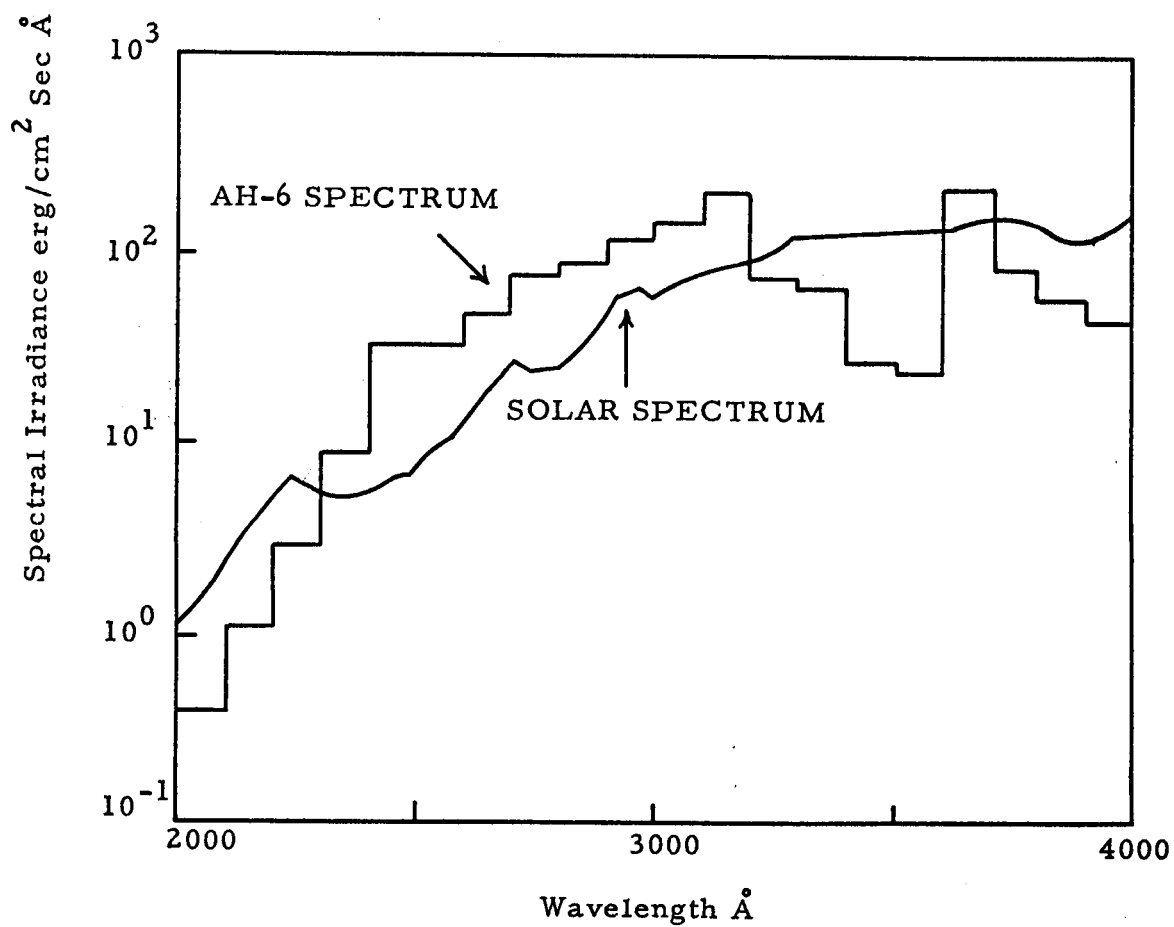
FIGURE 1 – COMPARISON OF SOLAR SPECTRUM
WITH SPECTRUM OF AH-6 LAMP
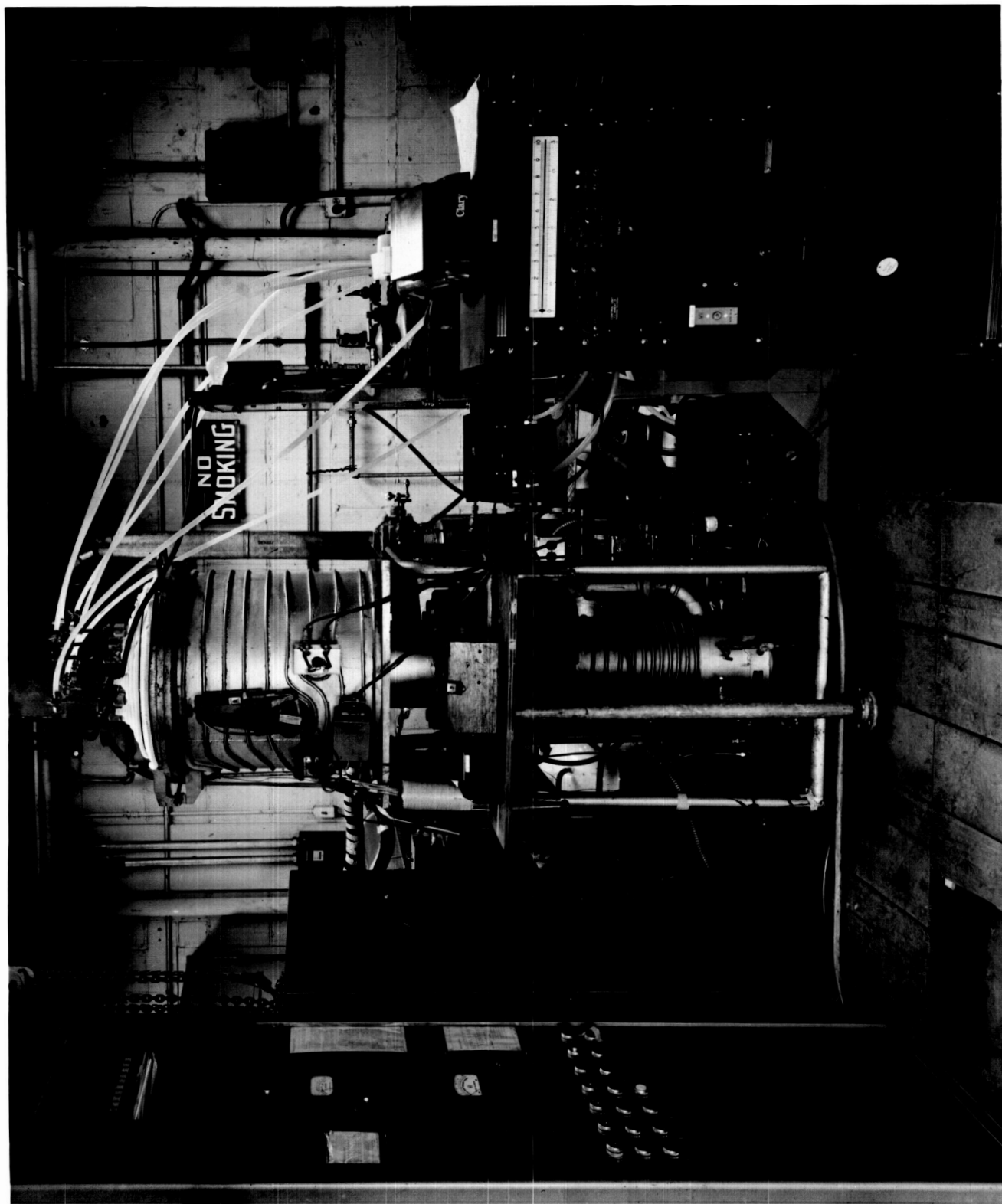
FIGURE 2 - SOLAR SIMULATION CHAMBER

Several types of sample turntables are available. The simplest is a sixteen-inch flat plate, suitable for use when no measurements are to be made in the chamber. Typically, this is used when the reflectivity of a number of materials are to be measured before and after a period of irradiation. The radiation intensity varies at different distances from the center of the turntable, so various acceleration factors are possible. Samples may be of many forms - pigmented or clear films, free or on any substrate, compacted or loose powders, even liquids, if the vapour pressure permits.

It should also be possible to measure changes in α/ϵ in situ, to determine the rate of yellowing, and perhaps to extrapolate to very long exposure times. According to the equation

$$A \; \alpha \; H = \epsilon \sigma \alpha A (T^4 - T_o^4)$$

$$\alpha/\epsilon = \frac{2\sigma (T^4 - T_o^4)}{H}$$

where A is the surface area (assuming a flat sample, only one side of which is irradiated

H is the incident radiation
σ is the Stefan-Boltzman constant 5.7×10^{-5} erg cm^{-2} sec^{-1} deg^{-4}
α is the absorptivity
ϵ is the emissivity
T is the sample temperature
T_o is the temperature of the cold sink.

It was recognized that our equipment was not a calorimeter, but it was hoped that at least the constancy of α/ϵ could be measured by monitoring the sample temperatures during irradiation. For this a skeleton turntable was constructed, with space for twelve samples mounted in clamps between the inner and outer rings. The turntable was rotated by a twelve-point Geneva drive and a 2-rpm fractional horsepower motor mounted in a welded housing open to the atmosphere through ventpipes to eliminate the problems attendant upon operating motors in a vacuum. Connection to the turntable is by a straight-through grease-packed seal. Rotary bellows seals were tried and discarded because of excessive and unreproducible back-lash. The samples are rotated in turn to the measuring position where a cam-actuated sliding block lowers a thermistor mounted on a spring arm against the sample in force during the idling periods in the cycle.

Several modifications and refinements of this equipment have been found necessary. In order to minimize heat transfer between the samples and the frame, the sample clamps have been equipped with glass-ball insulators, to prevent metal-to-metal contact. A radiation shield has been designed and installed to shadow the center and the rim of the turntable, thus permitting only the samples themselves to be irradiated. The center shield is the first-surface mirror used to reflect some of the radiation to the external monitoring thermopile. It is also necessary to shield the thermistor arm in order to obtain meaningful temperature measurements.

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Even when no measurements of α/ϵ are contemplated, it is desirable to have some indication of the sample temperatures. For non-cooled samples (as in this equipment) the $(T^4 - T_0^4)$ will increase linearly with the intensity, so care must be taken not to induce a simple thermal reaction. Present temperatures, at about 3x solar intensity, are about 150°F.

This chamber is mounted on a 10-inch oil diffusion pump, a National Research Corporation model H-10-SP with an approximate pumping speed of 4000 cfm at 10^{-4}mm. Pump down curves determined by the manufacturer are shown in Figure 3.

Auxiliary equipment includes the usual instrumentation for recording vacuum measurements from ionization gages and thermocouple gages and a cold trap for use with liquid nitrogen or mechanical refrigeration. The base plate contains a 10-inch pump port and accomodates chambers less than 28 inches in diameter.

In practice, the pump reaches 10^{-6} mm routinely in conjunction with this chamber. However, it is often desirable to sacrifice both pumping speed and ultimate vacuum in favor of more efficient trapping of pump oil. In some of our earlier experiments, the back streaming was very high; this condensed on the cold water jackets and photolyzed to a highly absorbent varnish which removed much of the ultraviolet radiation from the output of the lamps. This reduced the total radiation by about 20 % in 50 hours, with most of the loss concentrated in the important short wavelengths. Typical data for spectral output of the lamps before and after the deposition of this varnish are shown in Figure 4.

Most recently, a trap filled with Molecular Seive (Linde 13x) was used in series with an optical trap refrigerated with liquid nitrogen. This greatly reduced varnish deposition on the lamps.

The spectral distribution of the lamps was measured with a Seya-Namioka vacuum ultraviolet monochromator, manufactured by Jarrell-Ash.

III. ABSORPTIVITY AND EMISSIVITY MEASUREMENTS

Spectral reflectivities have been determined with a General Electric Recording Spectrophotometer, which employs approximately normal illumination and diffuse viewing of a sample surface, for the visible spectrum, 380 to 700 millimicrons, and an integrating sphere reflectometer of our own design for both the UV and IR regions. The latter incorporates a Perkin-Elmer quartz monochromator as a dispersing system along with appropriate sources and detectors. For the IR region, a ribbon filament incandescent lamp is a very satisfactory source and the detector is a lead sulfide photo-conductive cell. A mercury arc or hydrogen lamp is used for the UV range along with a photomultiplier detector.

Total normal emissivities have been measured with equipment shown in Figure 5. Test samples and a calibrated standard are mounted vertically in a sample tray and heated in a horizontal tubular furnace. The sample
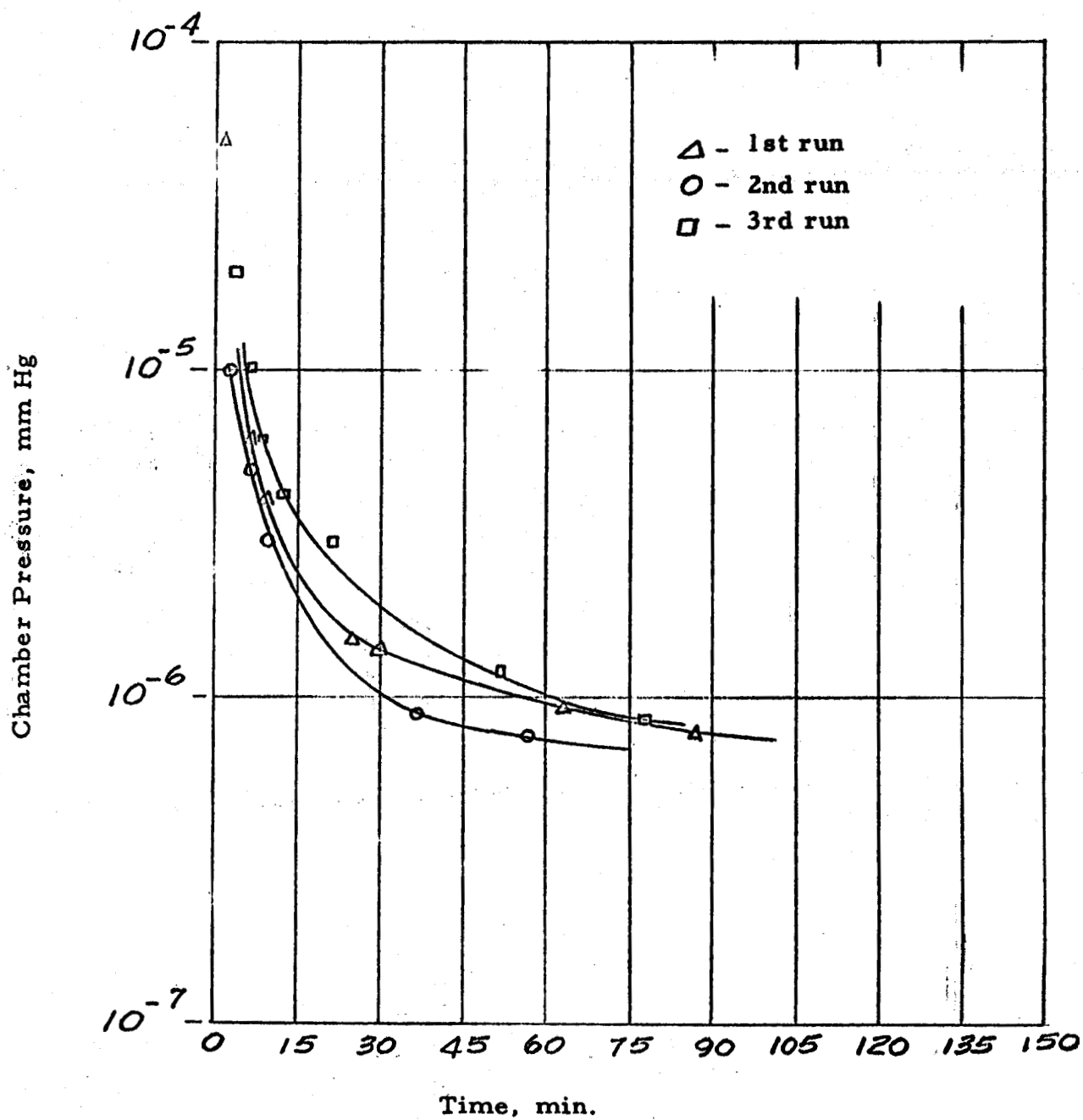
Fig. 3 TEST PUMP-DOWN DATA FOR NRC
        ENVIRONMENTAL CHAMBER
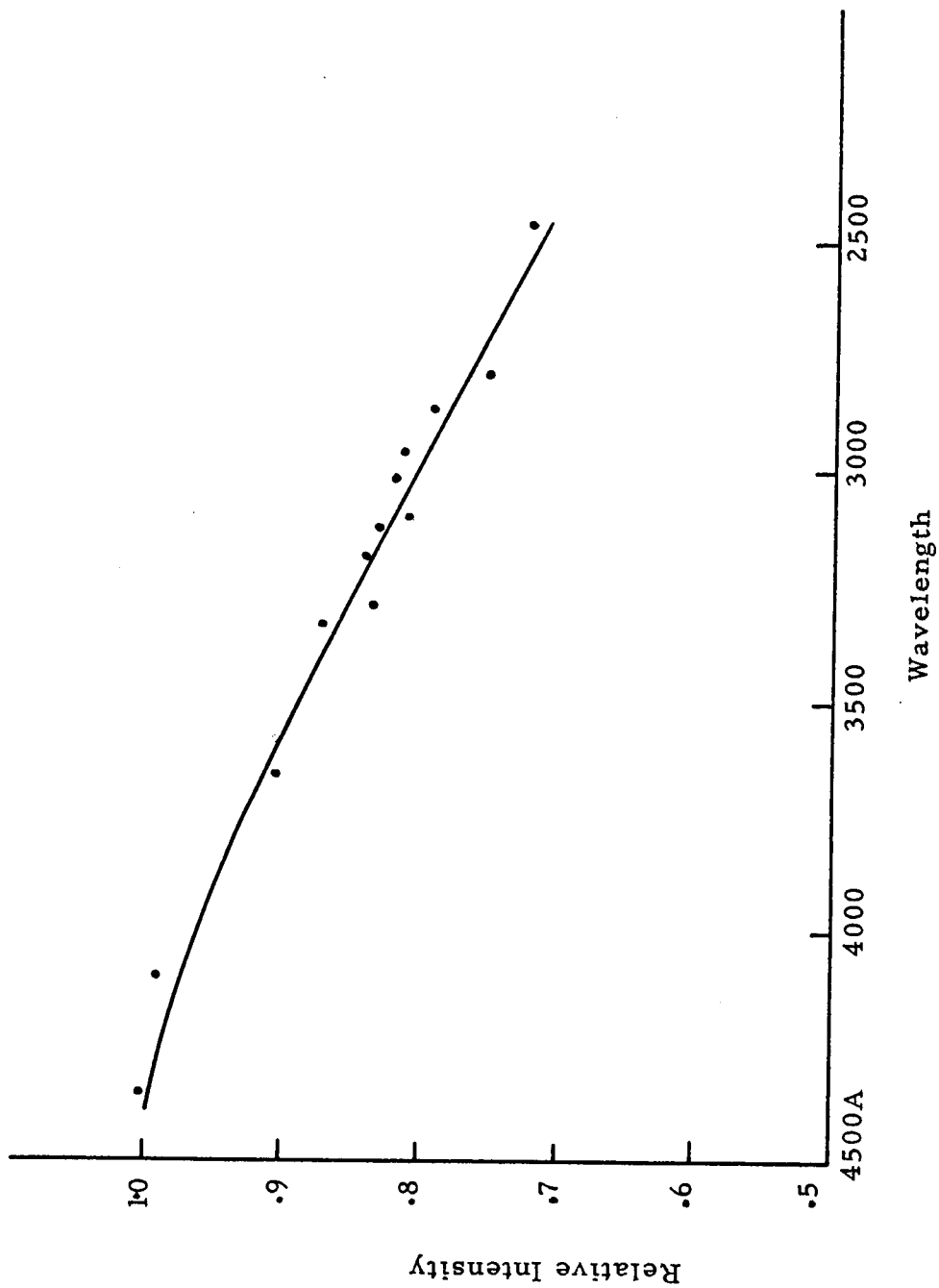
FIGURE 4 - RELATIVE INTENSITIES OF NEW AND AGED AH-6 LAMPS

Figure 5

EMISSIVITY APPARATUS

CERAMIC TUBE 2½" I.D., 3" O.D.

Rhodium alloyed Platinum Winding

K26 INSULATION BRICK

COOLING COILS

COOLING COILS

DETECTOR ASSEMBLY WITH CHOPPER ON CARRIAGE

BLACKBODY ASSEMBLY WITH CHOPPER 2¾" ON CARRIAGE

SAMPLE PORTS IN TROUGH

SAMPLE TROUGH

34"

14"

14"

8"

11"

tray is given a slow reciprocating motion parallel to the axis of the furnace by a mechanism not shown in the diagram. The total sample travel is about 14 in. which permits five samples in the tray to pass a viewing port twice per cycle to be viewed by a suitable detector. Comparison of signals from samples and calibrated standard yields the desired emissivity values. The specimens are viewed through a water cooled cone which is introduced with its nose close to the test surface at the time measurements are being made. This serves as a radiation shield and prevents radiant energy originating in the furnace walls from falling on the test surface and, subsequently, being reflected to the detector. Since samples and standard are heated in the same furnace, this method avoids the dangers of temperature errors associated with separately heated samples and standards. Working standards are calibrated against a carefully designed blackbody cavity and may be any thermally stable material. We use Pyroceram 9606 and polycrystalline silicon carbide.

IV. PREPARATION OF MATERIALS

A. Pigments

The initial criteria for pigments are that they be white and of high refractive index and purity. The most important factor in the choice of materials, i.e., stability to a space environment, was determined from the actual screening tests and from limited information in the literature. Acquisition of pigment materials from various firms therefore, has been a continuous activity in this program.

For the preliminary pigment screening tests, a powder preparation method which would yield samples suitable for both solar simulation exposure and optical measurements, was devised. The candidate powder is poured into a copper ring placed on a vellum-covered steel plate. A steel disc having a 1-1/2-inch diameter (equal to the inside diameter of the ring) is fitted into the ring, covering the pigment. A pressure of 10,000 psi applied on the steel disc results in the finished specimen illustrated in Figure 6. No binders or lubricants are used, thus obviating the possible effects of foreign materials. Powders which are not compactable into a cohesive body are placed in aluminum dishes for solar exposure. This precludes optical measurements and permits only visual observations as to color change.
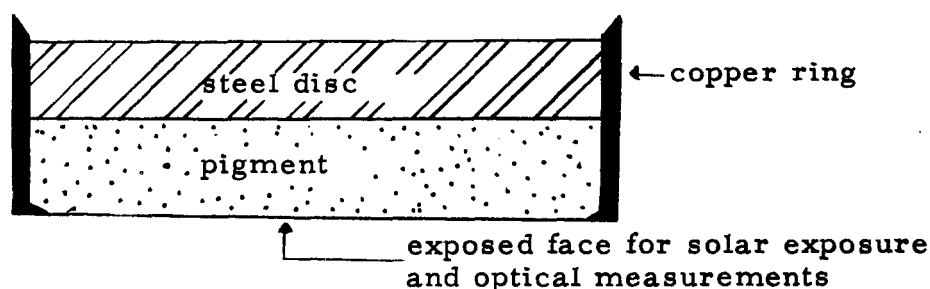
Figure 6 - Pigment Sample

B.1. Inorganic Vehicles

The inorganic binders which are of interest and possible suppliers are: alkali silicates (Sylvania Electric Products and Philadelphia Quartz), aluminum phosphate (Victor Chemical and Monsanto Chemical), and colloidal silica (DuPont and National Aluminate). The inorganic vehicles and pigments which showed the most promise are discussed further in subsequent sections on the results of solar exposures.

Vehicle samples for solar testing were prepared using the same techniques as for pigments with powders obtained by evaporating to dryness followed by an 800°F calcination. This may have been an unrealistic thermal treatment, however, since the paints must be cured below 300°F.

B.2. Organic Vehicles, Sources and Chemistry of Preparation

The organic coating vehicles which have been used in this research program, can be divided into the following major categories:

a. Semi-inorganic vehicles with organic "framing" groups
b. Fluorine-containing aliphatic resins
c. Organic polyesters
d. Epoxy resins
e. Miscellaneous vehicles, including organic resins with undisclosed composition or ratio of ingredients.

In the subsequent description, each organic vehicle is identified by a Roman numeral. Some of the vehicles have also Arabic numerals given to them by the manufacturer; for example, Kel-F Coating Latex No. 800. The Arabic numerals in parentheses refer to the chemical formula of the principal ingredient of the coating vehicle, such as tetrabutyl titanate (1). The formulae are absent if the manufacturer has not disclosed the exact chemical compositions of a vehicle; for example, Leonite No. 201.

a. Semi-Inorganic Vehicles

Semi-inorganic vehicles are summarized in Table 1.

Table 1

SEMI-INORGANIC VEHICLES WITH ORGANIC "FRAMING" GROUPS

No. of Vehicle	No. of Chemical Formula	Name	Thermal Stability
I	(1)	Tetrabutyl titanate	Distillable liquid
II	(2)	Polydibutoxytitanoxane	Stable over 300°F
III	(3)	Polydibutyltindibutoxy-titanoxane	Stable over 300°F
IV	(4)	RTV-11 Silicone Liquid Paste (with 1% Thermolite 12 curing agent)	Stable at 480°F
V	(4)	LTV-602 Silicone Liquid	Stable for continuous operation at 302°F, over 3000 hr at 347°F, 1000 hr or more at 392°F
VI	(5)	SE551N Silicone Gum Resin Dispersion	Operating range up to 500°F
VII	-	Silicone Resin No. 840 (used together with Acryloid C-10-LV, weight ratio 3:4)	Does not cure at 257°F, good adhesion after curing for 1 hr at 356°F
VIII	-	Silicone Resin No. 806A (contains 49% of solids)	Can be cured at 320°F or at 480°F; no greying, excellent adhesion

$$(CH_3CH_2CH_2CH_2O-)_4 Ti \qquad (1)$$

$$\left[\begin{array}{c} CH_3CH_2CH_2CH_2-O \\ \mid \\ -O-\!\!\!\!\!\!\!\!-Ti- \\ \mid \\ CH_3CH_2CH_2CH_2-O \end{array}\right]_n \qquad (2)$$

$$\left[\begin{array}{cc} CH_3CH_2CH_2CH_2-O & CH_2CH_2CH_2CH_3 \\ \mid & \mid \\ -O-\!\!\!-Ti-O-Sn- \\ \mid & \mid \\ CH_3CH_2CH_2CH_2-O & CH_2CH_2CH_2CH_3 \end{array}\right]_n \qquad (3)$$

$$\left[\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \end{array} \right]_n \tag{4}$$

$$\left[\begin{array}{c} CH_3 \\ | \\ -Si-O \\ | \\ CH_3 \end{array} \right]_n \left[\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ C_6H_5 \end{array} \right]_m \tag{5}$$
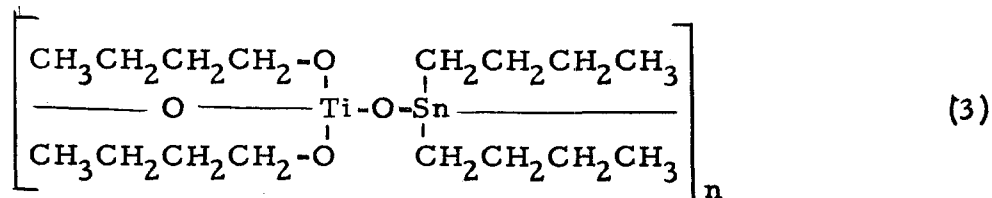
Tetrabutyl titanate (1) was purchased from Eastman Kodak Co. and purified by distillation. To (1) in toluene was added the calculated amount of water in ethanol to form (2), which was isolated as a colorless, viscous liquid after distilling the solvents and butanol formed in the reaction. Only about 8% of the product precipitated as a white solid and was removed. Two runs of this preparation were made.

Dibutyltin diacetate and (1) in equimolar amounts were heated to 130°C and then the calculated amount of butyl acetate was distilled. From the residue was isolated (3) as a yellow, transparent, moderately viscous liquid in a quantitative yield. Although oxygen and moisture were excluded during the preparation, the color probably was caused by some impurities.

RTV-11 Silicone Paste was obtained from General Electric Co. as a liquid polydimethylsiloxane (4) composition containing silica, calcium oxide and calcium carbonate as filler materials. Thermolite 12 was the curing agent used, which contains tin.

LTV-602 Silicone (General Electric Co.) is a transparent, liquid polydimethylsiloxane (4) containing no fillers. A lead-containing catalyst SRC-05 was used for the cure, for 24 hours at room temperature or for 2 hours at 150°F.

SE554N Silicone Gum is based on SE51 Gum (General Electric Co.), which is polydimethylsiloxane with some of the methyl groups along the siloxane chain replaced by phenyl groups (5). This gives a measure of disorder to the polymer molecule. For this reason, the resin is flexible and can be used from -150°F to +500°F.

Silicone Resins No. 840 and 806A were obtained from Dow Corning Co. The technical data sheets, supplied by the manufacturer, did not state the chemical structure of these resins.

b. Fluorine-Containing Aliphatic Resins

Fluorine-containing resins which were used as coating vehicles are summarized in Table 2.

Table 2

FLUORINE-CONTAINING ALIPHATIC RESINS

No. of Vehicle	No. of Chemical Formula	Name	Thermal Stability
IX	(6)	Teflon TFE High Purity Powder No. 7	Stable at 500°F; for short periods of time up to 621°F; sintering with some decomposition at 720 to 750°F, rapid loss of weight at 800 to 900°F and above
X	(6)	Teflon TFE Dispersion No. 30 (lower molecular weight than IX; aqueous dispersion at pH 10, containing 59-61% of solids incl. 5.5-6.5% of a non-ionic wetting agent).	After drying at 300°F no discoloration, no weight loss at 482°F, for shorter periods stable at 527 to 572°F
XI	(6)	Teflon TFE Clear Finish No. 852-201 (acidic aqueous dispersion containing 39-48% of solids incl. acid stabilizers and primers for adhesion to metals).	Milky white after drying at 212°F. Greyish color appears at 300 to 320°F. At higher temperatures fuses to a light tan film.
XII	(6)	Teflon TFE White Enamel No. 851-202 (aqueous dispersion; applied over Teflon TFE No. 850-202 aluminum primer coat).	The primer is yellow-orange when applied, turns brown when dried, and blue-gray after fusing; white enamel, applied over it, becomes greyish at 300°F, no weight loss at 482°F; marked discoloration at 700°F
XIII	(6)	Teflon TFE High Build Clear Finish No. 852-202 (applied over Teflon TFE No. 850-202 aluminum primer coat).	Up to 3 mils thick film can be applied without mud-cracking, if dried rapidly. Less discoloration by heating than for XII. As for XII only fair adhesion to aluminum after 300°F cure; good adhesion after 700°F cure

Table 2 (Cont.)

No. of Vehicle	No. of Chemical Formula	Name	Thermal Stability
XIV	(7)	Teflon FEP Dispersion No. 120 (aqueous dispersion at pH 10, containing 53 to 57% of solids and 5 to 7% of volatile, non-ionic and anionic wetting agents).	No discoloration at 300°F, but only fair adhesion. Continuous use possible at 400°F; good adhesion after curing at 650°F. Weight loss (0.3% per hr.) and slight discoloration at 700°F
XV	(8)	Kel-F Molding Powder No. 81 (high molecular weight, D.P. = 1300 to 1600, white powdered resin).	M.p. 414°F; little or no degradation by compression molding at 500°F; zero strength time decreases to one half of its initial value in 3 min. at 650°F upon injection molding and extrusion
XVI	(9)	Kel-F Resin No. 800	Can be hot-sprayed at 160°F in methyl isobutyl ketone and amyl acetate soln. or cold sprayed. Coating stable at 300°F, no discoloration
XVII	(9)	Kel-F Coating Latex No. KF 8213 (aqueous dispersion)	Stable at 300°F, but some mud-cracking as water evaporates
XVIII	(9)	Kel-F Coating Latex No. KF 8213 (modified dispersion in a ketone).	Stable at 300°F, no mud-cracking upon drying
XIX	(10)	Phosphonated Kel-F	Comparable thermal stability to XV except for yellowing
XX	(11)	Phosphonated Kel-F, after acidic hydrolysis	Comparable thermal stability to XV
XXI	(12)	Aminated Kel-F	Found unsuitable for pigmented coatings
XXII	(13)	Kynar No. L 18 (20-25% of polyvinylidene fluoride in dimethylacetamide).	Stable to 300°F; crystalline m.p. 340°F; preheat molding at 325 to 370°F; darkening at 400°F
XXIII	(14)	Exon No. 461	Stable at 300°F; degrades at 350°F
XXIV	(15)	Viton A	Can be cured at 300°F; no deterioration at 400°F for 100 days; decomposition products are evolved at over 500°F

Table 2 (Cont.)

No. of Vehicle	No. of Chemical Formula	Name	Thermal Stability
XXV	(15)	Viton B (cloudy solution in acetone or methyl isobutyl ketone).	Can be cured at 300°F; reasonably stable at 500°F for 20 days; remains longer elastic and deteriorates slower at 550°F than XXIV
XXVI	(15)	Viton B (semi-clear solution after partial settling of yellowish impurities and decantation).	Similar to XXV
XXVII	(15)	Viton B (clear, colorless solution, after complete settling of impurities during 10 days and decantation).	Better stability than that of the crude resin solutions XXV and XXVI

$$\left[-CF_2-CF_2-\right]_n \qquad (6)$$

$$\left[-CF_2-CF_2-CF_2-\underset{\underset{CF_3}{|}}{CF}-\right]_n \qquad (7)$$

$$\left[-CF_2-\underset{\underset{Cl}{|}}{CF}-\right]_n \qquad (8)$$

$$\left[-CF_2-\underset{\underset{Cl}{|}}{CF}-CF_2-CH_2-\right]_n \qquad (9)$$

$$\left[-CF_2-\underset{\underset{Cl}{|}}{CF}-\right]_n \left[CF_2-\underset{\underset{\underset{OCH_3}{|}}{O\leftarrow P-OCH_3}}{CF}-\right]_m \qquad (10)$$

$$\left[-CF_2-\underset{\underset{Cl}{|}}{CF}-\right]_n \left[CF_2-\underset{\underset{\underset{OH}{|}}{O\leftarrow P-OH}}{CF}-\right]_m \qquad (11)$$

$$\left[-CF_2-\underset{\underset{Cl}{|}}{CF}-\right]_n \left[CF_2-\underset{\underset{NH-CH_2CH_2CH_2OH}{|}}{CF}-\right]_m \qquad (12)$$

$$\left[-CH_2-CF_2-\right]_n \qquad (13)$$

$$\left[-CH_2-\underset{\underset{Cl}{|}}{C}H-CF_2-\underset{\underset{Cl}{|}}{C}F- \right]_n \qquad (14)$$

$$\left[-CH_2-CF_2-CF_2-\underset{\underset{CF_3}{|}}{C}F- \right]_n \qquad (15)$$
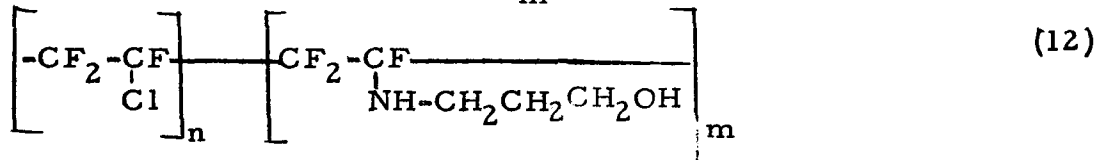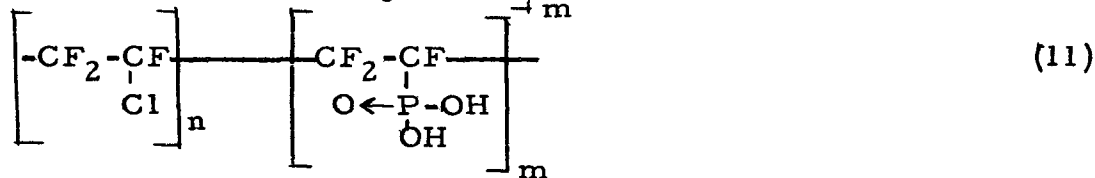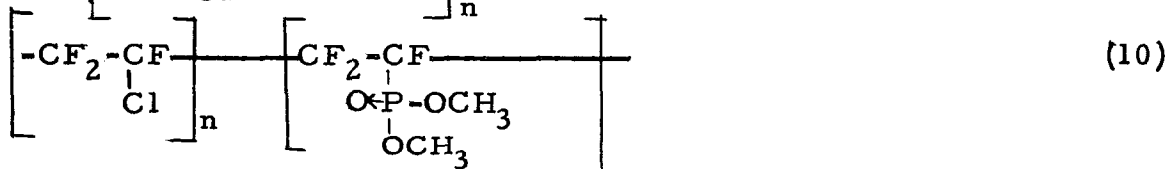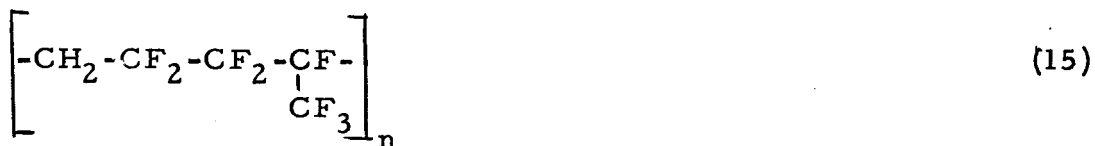
The fluorine-containing organic resins IX, X, XI, XII, XIII, XIV, XXIV, and XXV were purchased from E. I. du Pont de Nemours and Co.

Kel-F resins XV, XVI, and XVII were obtained from Minnesota Mining and Manufacturing Co.

The modified dispersion in a ketone XVIII was prepared from XVII by quenching the aqueous dispersion of Kel-F Coating Latex No. KF 8213 with liquid nitrogen, covering the solidified material with acetone, allowing to warm up, and decanting the supernatant solution. This process of water extraction could be repeated without further freezing.

An alternative was also successfully employed. The aqueous dispersion XVII was mixed mechanically with acetone at room temperature. Liquid nitrogen was added to the mixture, with continued stirring, until the mixture froze to a solid. The product was allowed to warm up, and the supernatant layer of aqueous acetone was decanted.

The purpose of the organic solvent was to extract water and to dilute the residual dispersion XVIII. Freezing inhibited the coagulation process in the transfer of resins from aqueous to non-aqueous medium. The residual dispersion XVIII could be dried over silica gel, calcium sulfate, and other drying agents which are unreactive with ketones. Higher molecular-weight ketones than acetone were also occasionally used to achieve the desired viscosity and to decelerate the evaporation upon spraying. Monowet 70% MO in concentrations of 0.01 to 0.1% by weight as well as other emulsification and dispersion agents could be also employed for the transfer of the dispersion from aqueous to non-aqueous medium.

Phosphonated Kel-F (XIX) was prepared in two runs by heating a mixture of XV and trimethyl phosphite. In the first run, Kel-F Molding Powder No. 81 was heated with an excess of trimethyl phosphite to 130°C, whereupon an exothermic and vigorous reaction started. The temperature increased spontaneously to 160°C, and the color of the mixture became orange-brown. According to British Patent 760, 144 to Pittsburgh Glass Co., the chloro groups of the polymer and trialkyl phosphites enter the Michaelis-Arbuzov reaction.

However, in this run the reaction took place predominantly on the surface of the powder granules, since the resin did not dissolve completely in the phosphite. The resin could be purified by dissolution in a mixture of

1, 1, 2, 2-tetrafluoro-3, 3, 4, 4-tetrachlorocyclobutane and toluene and reprecipitation by cooling or dilution with other organic solvents. In this manner, the yellow impurities were removed.

In the second run, the resin XV was dispersed in a mixture of xylenes, diisobutyl ketone and acetone. Trimethyl phosphite was added, and the reaction was started by warming the mixture to 78 to 85° C for 1 hour and at 60°C for 3 hours. The phosphonated resin XIX was partially soluble in the reaction mixture and an additional amount of acetone. By warming with concentrated hydrochloric acid and dilution with water, the ester groups were hydrolyzed and the resin XX was obtained as a white solid.

Kel-F Molding Powder No. 81 (XV) was heated with excess 3-aminopropanol in dispersion of concentrated aqueous sodium hydroxide, and then water was added. The precipitated resin XXI was found unsuitable for pigmented coatings.

Kynar No. L 18 (XXII) was acquired from Pennsalt Chemicals Corp., and a sample of Exon 461 (XXIII) was obtained from Firestone Plastics Co.

The solutions of Viton B (XXVI and XXVII) were prepared by partial or complete settling of the initial cloudy solution (XXV) and decantation. As discussed later in detail, the clear solution (XXVII) gave a resin film with better properties of stability than XXV or XXVI.

c. Organic Polyesters

Organic polyesters which were used as coating vehicles are summarized in Table 3. The thermal stability limits were not determined. The polyesters were cured with 1% by weight of benzoyl peroxide for 16 hours at 176°F; 8 hours at 212°F; and 16 hours at 248°F. Occasionally shorter curing cycles were used; XXXVI was applied at room temperature.

Table 3

ORGANIC POLYESTERS

No. of Vehicle	No. of Chemical Formula	Name
XXVIII	(16)	Monoallyl maleate
XXIX	(17)	Allyl trimethallyl phosphonylsuccinate
XXX	(18)	Dodecaallyl pentaerythrityl tetra-(phosphonyl-succinate)
XXXI	(19)	Chlorendate and maleate polyester
XXXII	(20)	Phosphonated chlorendate and maleate polyester
XXXIII	(21,22)	Glycol tetrachlorophthalate and maleate polyester
XXXIV	(22,23)	Phosphonated glycol tetrachlorophthalate and maleate polyester
XXXV	(18,22, 23)	Phosphonated glycol and pentaerythritol tetrachlorophthalate, and maleate polyester
XXXVI	——	Cellulose acetate butyrate

$$H\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\diagdown_{\underset{H}{\diagup}C=C\overset{\diagup}{\underset{\diagdown H}{}}}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2CH\text{=}CH_2 \qquad (16)$$

$$CH_2\text{=}CH\text{-}\underset{|}{\overset{CH_3}{CH}}\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{|}{CH}\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH\text{=}CH_2 \qquad (17)$$

$$CH_2\text{=}CH\text{-}CH\text{-}O\text{-}\underset{\underset{O}{\downarrow}}{P}\text{-}O\text{-}CH\text{-}CH\text{=}CH_2$$

$$\underset{CH_3}{|} \qquad \underset{CH_3}{|}$$

$$C\Big[\text{-----}CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\underset{|}{CH}\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}CH_2\text{-}CH\text{=}CH_2 \qquad (18)$$

$$CH_2\text{=}CH\text{-}CH_2\text{-}O\text{-}\underset{\underset{O}{\downarrow}}{P}\text{-}O\text{-}CH_2CH\text{=}CH_2\Big]_4$$

$$C \left\{ CH_2O \left[\overset{O}{\overset{\|}{C}} - CH=CH - \overset{O}{\overset{\|}{C}} - OCHCH_2CH_2O \right]_2 \overset{O}{\overset{\|}{C}} - CH=CH - \overset{O}{\overset{\|}{C}} - OH \right\}_3 \quad (19)$$

with pendant chain:

$$CH_2 \quad O \left[\overset{O}{\overset{\|}{C}} - CH=CH - \overset{O}{\overset{\|}{C}} - O - CH - CH_2CH_2O \right]_2 \overset{O}{\overset{\|}{C}} - \quad CH_3$$

containing:

Cl-substituted bicyclic ring (Cl, Cl, Cl, Cl, Cl, Cl) with H, H and $\overset{O}{\overset{\|}{C}}-OH$

$$(20)$$

$$C \left\{ CH_2O \left[\overset{O}{\overset{\|}{C}} - CH=CH - \overset{O}{\overset{\|}{C}} - O - CH - CH_2CH_2 - O \right]_2 \overset{O}{\overset{\|}{C}} - CH - CH_2 - \overset{O}{\overset{\|}{C}} - OCH_2CH=CH_2 \right\}_3$$

with $O \leftarrow P - OCH_2CH=CH_2$ and $O - CH_2CH=CH_2$

$$HOCH_2CH_2O - \overset{O}{\overset{\|}{C}} - \underset{(Cl,Cl,Cl,Cl \text{ ring})}{} - \overset{O}{\overset{\|}{C}} - O - CH_2CH_2 - O - \overset{O}{\overset{\|}{C}} - CH=CH - \overset{O}{\overset{\|}{C}} - OH \quad (21)$$

$$HO \left[CH_2CH_2 - O - \overset{O}{\overset{\|}{C}} - CH=CH - \overset{O}{\overset{\|}{C}} - O \right]_2 H \quad (22)$$

$$HO - CH_2CH_2 - O - \overset{O}{\overset{\|}{C}} - \underset{(Cl,Cl,Cl,Cl \text{ ring})}{} - \overset{O}{\overset{\|}{C}} - OCH_2CH_2 - O - \overset{O}{\overset{\|}{C}} - CH - CH_2 - \overset{O}{\overset{\|}{C}} - OCH_2CH=CH_2$$

$$CH_2 = CH - CH_2 - O - \overset{\downarrow O}{\underset{}{P}} - O - CH_2CH=CH_2 \quad (23)$$

The unsaturated and phosphonated esters and polyesters XXVIII-XXXV were made at the Armour Research Foundation by N. E. Boyer in an earlier investigation of the phosphonation of unsaturated acids by tertiary phosphites. All preparations were carried out under nitrogen atmosphere.

Equimolar amounts of allyl alcohol and maleic anhydride were mixed at room temperature, kept overnight at 25°C, and the colorless solution was heated to 120°C for 1 hr to form a colorless liquid, monoallyl maleate (XXVIII); calcd., acid no. 359; found, 358.

Trimethallyl phosphite was added dropwise with stirring, to an equimolar amount of XXVIII. The mixture warmed up spontaneously to 100°C and was cooled externally to keep it below this temperature. Then the mixture was heated to 100°C for 2 hrs. The product XXIX was a colorless liquid; acid no. 0; found, 0.8.

Pentaerythritol, 5 moles; maleic anhydride, 20 moles; and fumaric acid, 2 moles, were mixed at room temperature and gradually heated up with stirring, to 109°C in 8 hr. A homogeneous, liquid mixture, milky white and cloudy, was formed; it contained mainly pentaerythrityl tetramaleate and a small amount of fumaric acid. Calcd. acid no. for pure pentaerythrityl tetramaleate, 425; for the above product, 469; found, acid no. 435.

To one half of the above mixture containing mainly pentaerythrityl tetramaleate was added dropwise, with stirring, 11 moles of triallyl phosphite at 69°C to 100°C during 9 hrs. A clear, pale greenish yellow polyester XXX was formed. Calcd., acid no. 15.3; found, 12.4. The completeness of the addition reaction according to the formula (18) was indicated by the low acid number and absence of the characteristic phosphite odor. Similar observations were made in the other phosphonation reactions.

1,3-Butanediol, 8 moles; maleic anhydride, 3 moles; chlorendic acid, 1 mole; and pentaerythrityl tetramaleate, 1 mole, were mixed at 25°C and cooked at a reduced pressure at 130°C for 6 hours. Excess 1,3-butanediol (2.88 moles) was added and distilled again in the course of the reaction, as the cooking in an oil bath was continued at a reduced pressure for 24 hours at up to 195°C residue temperature. The calculated amount of water was also distilled. For the residue, calcd., acid no. 0; found, 2. This product was stirred and reacted with 4 moles of maleic anhydride for 4 hours at up to 107°C to prepare the polyester XXXI in a quantitative yield. Calcd., acid no. 199.5; found, 199.6.

To the polyester XXXI, 1 mole, was added dropwise, with stirring, 3.6 moles of triallyl phosphite during 1 hr, while the temperature increased spontaneously to 80°C. The phosphonation reaction was completed by heating for 6 hours to 72°C, by addition of 0.8 mole of XXVIII and by reheating to 140°C for 2 hours. Calcd., acid no. of the polyester XXXII, 22; found, 21. It should be noted that the formula (20) represents just one of the several molecular species present in the polyester XXXII. Thus, for example, about half of the polyester molecules should contain four instead of three phosphonyl-succinate groups.

From a mixture of 1 mole of tetrachlorophthalic anhydride, 1 mole of maleic anhydride, and 4 moles of ethylene glycol, the calculated amount of water was distilled at a reduced pressure in 22 hours at up to 193°C. The product was obtained in 99% yield, and contained an equimolar mixture of bis-(2-hydroxyethyl) maleate and bis-(2-hydroxyethyl) tetrachlorophthalate. This product was reacted with 2 moles of maleic anhydride for 11 hours at up to 130°C to form the polyester XXXIII which contained (21), (22), as well as some other molecular species.

The phosphonation of one half of the product XXXIII with 0.5 mole of triallyl phosphite at up to 87°C in 1.5 hour and heating to 130°C for 1.5 hour formed in 98% yield the polyester XXXIV, which can be represented by typical molecular species (22) and (23).

The polyester XXXV was obtained by mixing equal weights of the resins XXX and XXXIV for 1.5 hour at 130°C until a homogeneous blend was established.

Cellulose acetate butyrate (XXXVI) was obtained as a film from Auburn Plastics Co. It was dissolved in a mixture of methyl isobutyl ketone and acetone for applications in coatings.

d. Epoxy Resins

The epoxy resins used in this research program are summarized in Table 4.

Table 4

EPOXY RESINS

No. of Vehicle	No. of Chemical Formula	Name of Resin and Manufacturer	Curing Conditions
XXXVII	(24)	Kopoxite No. 159, used with Hardener EP (Koppers Co.)	Room Temperature
XXXVIII	-	Epoxy Coating Compound No. Y-5-1 (Magnolia Plastics Co.)	302°F for 0.5 hour
XXXIX	-	Epoxy Enamel No. 6301 (American Marietta Co.)	320°F for 1 to 2 hours
XL	-	Epoxy Coating No. 345 T (Homalite Corp.)	320°F for 0.5 hour

$$CH_2\text{-}CH\text{-}CH_2\text{-}O \text{—} \underset{O}{\bigcirc} \text{—} O\text{-}CH_2\text{-} CH\text{-}CH_2 \qquad (24)$$
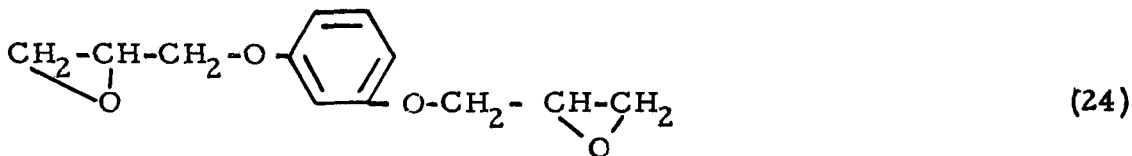
e. Miscellaneous Organic Paint Vehicles

The miscellaneous paint vehicles listed in Table 5 include organic resins which have a chemical composition undisclosed by the manufacturer, or which do not fit in the above discussed four classes of organic resins.

Table 5

MISCELLANEOUS ORGANIC PAINT VEHICLES

No. of Vehicle	Name of Resin and Manufacturer	Curing Conditions
XLI	Acrylic Primer No. A29950 (Bradley Vrooman Co.)	266°F for 10 min.
XLII	Phenolic Primer No. P-403 and Phenol-Formaldehyde White Enamel No. W-307 (Heresite Co.)	Primer: 320°F for 10 min. Enamel: 320°F for 15 hours
XLIII	Leonite 201-S (Leon Chemical Industries, a silicone-epoxy modified acrylic resin).	Cured at 230°F for 30 min. and heat-aged at 320°F for 20 hours.
XLIV	Rhoplex B 60A (Rohm x Haas Co.)	Dried at 266°F for 5 min.
XLV	Polyvinylpyrrolidone No. K 60 (General Aniline Corp.)	Dried at 230°F for 5 min.
XLVI	Cellulose Gum No. 7-MP (Hercules Co.)	Dried at 257°F for 1 hour

C. 1. Coatings and Primers, Inorganic and Combinations of Organic and Inorganic

Paint formulations were prepared utilizing as high a pigment-to-binder ratio as was compatible with good physical properties; satisfactory spraying viscosity was achieved by the addition of varying amounts of water. Early in the program the constituents were mixed by a combination grinding-mixing action employing an agate mortar and pestle. More recent methods are hand-shaking or ball-milling of the compositions with porcelain balls.

The vehicle which has been used almost exclusively in this program has been PS7, a high purity 35% solution of potassium silicate ($1K_2O/3.31 SiO_2$) marketed by Sylvania Electric Products Inc. The emphasis on silicate binders was dictated by reaction of monoaluminum dihydrogen phosphate with aluminum and the poor strength and solar instability of colloidal silica, the two other prime binder possibilities.

Substrates for the paints were prepared from Type 6061-T6 aluminum in sizes of 1 x 3 x 1/16-inch for environmental tests and 1-3/4 x 1-3/4 x 1/4-inch for emittance measurements. Both sizes are suitable for reflectance determinations. Some AZ31 alloy magnesium specimens were also prepared in the 1 x 3 x 1/16-inch size.

Spray painting was conducted with a Paasche Type AUTF air-brush; limited brush painting utilized conventional camel hair brushes. Aluminum pieces were grit blasted with 40 mesh SiC prior to paint application to promote adhesion. Thickness of the paint was decreed by adequate covering or hiding of the substrate. Since hiding power is a function of both particle size and refractive index, thicknesses varied with the pigments.

Moderately mild curing conditions were used for most of the paints to minimize possible crazing from too rapid drying. Samples were generally air dried overnight prior to a 24 hour 250°-300°F heat cure.

Rather high liquid requirements were encountered for some of the pigments due to several reasons: extremely fine particle size ($<$ 1 micron), high surface area, and the thixotropic nature of the material. This often led to crazing and/or chalky coatings. On the other hand, coarse pigments presented difficulty of spraying and poor paint textures. It is apparent that modification of the physical properties of pigments would yield improved paints; however, such refinements were deferred until the screening tests could demonstrate the materials which would merit more intensive study.

Composite inorganic-organic coatings are of interest for combining the advantageous properties of the respective layers, i.e., space stability of a ceramic paint and good physical properties and high emissivity of a polymer. The organic also provides a protective film on aluminum for aluminum phosphate paints.

Wetting of various organic coatings with silicate formulations was aided by a very light preblasting with fine silicon carbide. An alternate method of application for phosphate paints was to smear the organic with a thin coating of the inorganic followed by drying, producing a wettable adherent film. The most satisfactory double coating to date has been realized using an underlayer of ZnO-pigmented Leonite 201S, a silicone-epoxy modified acrylic.

Other methods have been attempted to obtain improved wetting. Incorporation in ceramic paints of water soluble organic surface tension depressants volatile below 300°F, has been unsuccessful; morpholine, acetic acid and N-propylamine as well as alcohols all gel the silicate solution. A monomolecular layer of a wetting agent, "Ultrawet," on the primer permitted excellent wetting but acted as a parting agent on heat curing. Some polymers were prepared incorporating asbestos fibers to render them more receptive to the ceramic formulations. Wettability was only somewhat improved, however, and a definite deficiency of this technique was the difficulty encountered in achieving a desirable paint texture which tended to follow the uneven surface of the undercoat.

A common difficulty encountered with combination coatings was a tendency for the ceramic to craze on curing, a fault less pronounced for the phosphate composition than for the silicate. The crazing is probably due to non-uniform shrinkage resulting from incomplete wetting.

C.2. Coatings and Primers, Organic

a. Preparation

Preparation of coatings containing organic vehicles is summarized in Table 6. All coatings were applied to one surface of an aluminum plate, which had the dimensions of 3 x 1 x 1/16 in. In a few cases, where the coatings were applied to a glass plate of similar dimensions, this fact is noted in the right side column of Table 6. Glass plates were occasionally used to determine whether the darkening of some coatings by thermal treatment is due to a chemical reaction with aluminum or to a reaction within the coating.

Two systems of numbering the samples of organic coatings were used. Coatings No. 1-199 were numbered in a chronological order of preparation, while another investigator labeled his coating specimens according to the notebook and page number, starting with No.401-1 (fourth notebook of this project, p.1, formulation No. 1 on that page).

The numbers of paint vehicles (Roman numerals) are the same as indicated in Tables 1 to 5.

The ratio of pigments to paint vehicles in a coating was obtained by dividing the weight of the vehicle used through the weight of pigment in grams. The solvents and dispersing agents which evaporated during the drying or thermal treatment were not included in this ratio.

Solvents, dispersion agents, and primers are mentioned in Table 6, if they were added during the formulation of the paint before spraying. They were omitted from Table 6 if they were included in the commercial composition by the manufacturer, in which case, if known, they have been already indicated in the preceding tables. Thus, it has been indicated in Table 2 that X contained, besides the resin, 52-61% of water, acid stabilizers and primers for adhesion to metals. Also, it has been already mentioned that to the polyester vehicles listed in Table 3, except XXXVI, was added 1% by weight of benzoyl peroxide before the spraying and cure.

A typical method of preparation of coatings was to disperse the resin in a solvent by shaking or rotating in a plastic container with glass or silica beads; to mix the dispersion or solution with a pigment, and to spray it with a compressed air spray gun in one or several layers until the aluminum surface was covered completely and did not shine through after drying.

If other methods of application were used, such as brushing or dip-coating, they have been indicated in the right hand column of Table 6. Room temperature cure (R. T.) or other curing conditions (°F and hours) also have been specified there.

Some coatings which were found unsatisfactory during the preparation and were discarded, were not included in Table 6.

Table 6

PREPARATION OF COATINGS CONTAINING ORGANIC VEHICLES

No. of Coating	No. of Vehicle	Pigment	Ratio of Pigment to Vehicle	Solvents or Dispersion Agents Added Before Use	Curing Conditions (°F) and Application Method if other than Spraying
1	III	ZrO_2	1	Toluene	R. T.
2	III	ZrO_2	1	Toluene	R. T.
3	IX	ZrO_2	1	Freon-112	R. T.
4-6	I	ZrO_2	1;0.7;0.7	Freon-112; none; toluene	R. T.
7	XXVIII	ZrO_2	0.8	Toluene	194°, 248°, 8, 16 hrs
8	XXIX	ZrO_2	0.5	-----	176°, 230°, 16, 5 hrs
9	XXX	ZrO_2	0.5	Acetone	194°, 248°, 8, 16 hrs
10	XXXII	ZrO_2	0.5	Acetone	194°, 248°, 8, 16 hrs
11	XXXI	ZrO_2	0.5	Acetone	194°, 248°, 8, 16 hrs
12	XIX	ZrO_2	3.3	Freon-112	R. T.
13	X	--	--	--	752° 1.2 hrs
14	X	--	--	--	320°, 419°, 1, 1.5 hrs
15	X	ZrO_2	0.62	--	650° 1.2 hrs
16-17	X	ZrO_2	0.62	--	320°, 419°, 1, 1.5 hrs (No. 17 painted)
18-19	II	ZrO_2	0.18	--	R. T.
20	X	--	--	--	752° 0.5 hrs (dip-coated)
21	X	--	--	--	650° 1.2 hr (dip-coated)
22-23	X	--	--	--	550°, 600°, 650°, 0.25, 0.25, 0.25 hrs
24	X	--	--	--	R. T.
25-26	X	$CaSiO_3$	1; 0.5	--	As for No. 22
27	X	$CaSiO_3$	0.5	--	R. T.
28-29	X	ZrO_2	0.66	--	As for No. 22
30-31	X	ZrO_2	0.66; 0.5	--	R. T.
32	X	ZrO_2	0.5	--	As for No. 22
33	X	ZrO_2	0.5	--	R. T.
34-35	X	Al_2O_3	0.1	--	R. T.
36-37	XI	Al_2O_3	0.13	Water	550°, 0.25 hr
38	X	--	--	--	248°, 650°, 1, 1, hr (dip-coated)

Table 6 (cont.)

No. of Coating	No. of Vehicle	Pigment	Ratio of Pigment to Vehicle	Solvents or Dispersion Agents Added Before Use	Curing Conditions (°F) and Application Methods if other than Spraying
39	II	ZrO$_2$	0.5	--	320° 16 hrs
40	II	ZrO$_2$	0.5	--	R. T.
41–42	II	ZrO$_2$	0.5	--	320° 16 hrs
43	XI	Al$_2$O$_3$	0.13	Water	R. T.
44–45	XI	CaSiO$_3$	0.9	Water	320°, 550° 16, 0.25 hrs
46	XI	CaSiO$_3$	0.9	Water	R. T.
47–48	XI	ZrO$_2$	0.9	Water	As for No. 44
49	XI	ZrO$_2$	0.9	Water	R. T.
50	X	Al$_2$O$_3$	0.1	--	As for No. 22
51–53	XXXIII	--	--	Acetone	176°, 239°, 16, 8 hrs
54–55	XXXIII	CaSiO$_3$	0.25	Acetone	As for No. 51
56–58	X	--	--	--	320°, 16 hrs
59	X	--	--	--	(Sprayed on glass) 320°, 16 hrs
60–62	XI	--	--	--	(Poured on glass) 320°, 16 hrs
63	XI	--	--	--	(Sprayed on glass) 320°, 16 hrs
64	XV	--	--	Tetrachlorotetrafluoro-cyclobutane	(Poured on glass) R. T. (painted)
65	XV	--	--	Tetrachlorotetrafluoro-cyclobutane	320° 64 hrs (painted)
66–68	X	--	--	--	320° 16 hrs
69–70	XXXIII	--	--	Acetone	176°, 239° 16, 72 hrs
71	XXXIII	--	--	Acetone	As for No. 69 (Poured)
72–73	XXXIII	CaSiO$_3$	0.5	Acetone	As for No. 69 (painted)
74	XXXIII	CaSiO$_3$	0.5	Acetone	As for No. 69
75	XIX	ZrO$_2$	1.5	Tetrachlorotetrafluoro-cyclobutane	R. T. (painted)
76–79	XXXIII	CaSiO$_3$	0.43	Acetone	176°, 212°, 248°, 16, 8, 16 hrs
80–83	XXXIII	ZrO$_2$	0.43	Acetone	As for No. 76

Table 6 (cont.)

No. of Coating	No. of Vehicle	Pigment	Ratio of Pigment to Vehicle	Solvents or Dispersion Agents Added Before Use	Curing Conditions (°F) and Application Methods if other than Spraying
84-86	XXXIII	Al$_2$O$_3$	0.37	Acetone	As for No. 76
87-89	XXXIV	CaSiO$_3$	0.43	Acetone	As for No. 76
90-92	XXXV	--	--	Acetone	As for No. 76
93-95	XXXV	ZrO$_2$	0.35	Acetone	As for No. 76
96-97	XXXIV	--	--	Acetone	As for No. 76
98-99	XXXVII	ZrO$_2$	0.5	"	R. T.
100-101	XXXVII	ZrO$_2$	0.5	"	R. T. (painted)
102-106	XXXVII	Al$_2$O$_3$	0.5	"	R. T.
107-110	XXXVII	Al$_2$O$_3$	0.5	Acetone	R. T.
111-113	XVI	ZnO	0.6	Methyl isobutyl ketone and amyl acetate	R. T.
114	XVI	ZnO	0.5	Methyl isobutyl ketone and amyl acetate	R. T. 72 hrs, 248° 24 hrs
115-118	XVI	ZnO	0.5	Methyl isobutyl ketone and amyl acetate	R. T.
119	XVI	ZnO	0.5	Methyl isobutyl ketone and amyl acetate	R. T. 72 hrs. 248° 72 hrs
120	XVI	ZnO	0.5	Methyl isobutyl ketone and amyl acetate	R. T.
121	XIV	ZnO	0.4	--	248° 72 hrs
122	XIV	ZnO	0.4	--	R. T.
123	XXII	ZnO	1	Methyl isobutyl ketone	R. T.
124-127	XXIII	ZnO	1	Methyl isobutyl ketone	R. T. (poured)
128	XXIII	ZnO	1	Methyl isobutyl ketone	248° 72 hrs (poured)
129	XXII	ZnO	1	Methyl isobutyl ketone	248°, 311° 30, 20 min
130	XXII	ZnO	1	Methyl isobutyl ketone	311° 10 min
131-133	XXII	ZnO	1	Methyl isobutyl ketone	R. T. 24 hrs, 302° 10 min
134	XXII	ZnO	1	Methyl isobutyl ketone	R. T. 18 hrs, 248° 30 min
135-140	XVI	ZnO	0.6	Methyl isobutyl ketone and amyl acetate	R. T.

Table 6 (cont.)

No. of Coating	No. of Vehicle	Pigment	Ratio of Pigment to Vehicle	Solvents or Dispersion Agents Added Before Use	Curing Conditions (°F) and Application Methods if other than Spraying
141	XVI	ZnO	1	Methyl isobutyl ketone and amyl acetate	R. T.
142-144	XVI	CaSiO$_3$	0.6	Methyl isobutyl ketone and amyl acetate	R. T.
145	XVI	--	--	Methyl isobutyl ketone and amyl acetate	R. T., on grit-blasted Al surface
146-147	XVI	--	--	Methyl isobutyl ketone and amyl acetate	R. T., on smooth Al surface
148-153	XVI (54%) and IX (14%)	ZnO 32%	0.48	Methyl isobutyl ketone and amyl acetate	R. T.
154-155	XXIII	ZnO	0.5	Methyl isobutyl ketone, butyl acetate, xylene, toluene	R. T.
156-157	XXII	ZnO	5	Acetone	R. T. 16 hrs, 356° 0.5 hr, quenched in H$_2$O
158-159	XXV	ZnS	5	Acetone and methyl isobutyl ketone	185°, 257° 24, 24 hrs
160	XVI	ZnS	5	Methyl isobutyl ketone and amyl acetate	R. T., then 300°
161-163	XXV	ZnO	5	Methyl ethyl ketone and 0.003% benzoyl peroxide	185°, 257° 24, 24 hrs
164	XXIII	ZnS	4	Methyl isobutyl ketone, butyl acetate, xylene and toluene	R. T.
165	XXIII	ZnS	4	Methyl isobutyl ketone, butyl acetate, xylene and toluene	R. T., then 150° 6 hrs
166	XII	--	--	--	300°
167-168	XII	--	--	--	700°
169	XIII	ZnO	0.67	Water	300°
170-171	XIII	ZnO	0.67	Water	300°, 750°
172-173	XXIV	ZnO	4	Acetone, methyl isobutyl ketone, and 0.01% benzoyl peroxide	R. T.

Table 6 (cont.)

No. of Coating	No. of Vehicle	Pigment	Ratio of Pigment to Vehicle	Solvents or Dispersion Agents Added Before Use	Curing Conditions (°F) and Application Methods if other than Spraying
174-177	XXIV	ZnO	4	Acetone, methyl isobutyl ketone, and 0.01% benzoyl peroxide	R. T., then 212° 72 hrs
178-179	XVI	ZnS	5	Methyl isobutyl ketone, amyl acetate, and 0.004% to 0.008% Uvinul No. 490 (Antara Chemical Co.)	R. T. then 300°
180	XXVI	ZnO	5	Methyl ethyl ketone and 0.003% benzoyl peroxide	185°, 257° 24, 24 hrs
181	XXVII	ZnO	4	Methyl ethyl ketone and 0.003% benzoyl peroxide	185°, 257° 24, 24 hrs
182	XXVI	ZnO	5	Methyl ethyl ketone and 0.003% benzoyl peroxide	185°, 257° 24, 24 hrs
183-184	XVII	ZnO	1	Water	R. T., then 300°
185-186	XVII	ZnO	1.5	Water	R. T., then 300°
187-188	IV	--	--	--	R. T.; then 300°
189	XXVII	ZnO	4	--	R. T., then 300°
190-191	XXVII	ZnO	4	Methyl ethyl ketone and 0.01% Uvinul No. 490	R. T., then 300°
192-193	IV	ZnO	1	Methyl ethyl ketone and 0.02% Uvinul No. 490	R. T., then 300°
194-196	XVIII	ZnO	5	Butyl acetate	R. T., then 300°
197-198	V	ZnO	5	Acetone	75°, 248°, 302°, 16, 4, 4 hrs
199	VI	ZnO	3.4	Toluene	R. T. then 300°
401-1	XLI	--	--	--	R. T., then 266° 10 min (dip-coated)
401-2	XLI	--	--	--	R. T., then 266° 10 min (sprayed)
401-3	XXXVIII	--	--	--	R. T., then 302° 30 min
401-4	XXXXIX	--	--	--	320° 1 hr
401-5	XL	--	--	Asbestos fibers dusted on	320° 30 min
401-6	XLII	--	--	--	Prime: 320° 10 min Enamel: 320° 15 hrs
402-1	XLIII	--	--	--	230° 30 min: 320° 20 hrs
402-2	XLIII	--	--	Asbestos fibers dusted on by flocking gun	230° 30 min, 320° 18 hrs.

Table 6 (cont.)

No. of Coating	No. of Vehicle	Pigment	Ratio of Pigment to Vehicle	Solvents or Dispersion Agents Added Before Use	Curing Conditions (°F) and Application Methods if other than Spraying
402-3,4	XLIII	ZrO$_2$	0.67	--	266° 30 min
402-5,6	XLIII	ZrO$_2$	0.67	--	266° 30 min; 320° 15 hrs
403-1	XLIII	TiO$_2$	1.25	Acetone	266° 30 min; 257° 24 hrs
403-2	XLIII	TiO$_2$	1.25	Acetone	266° 30 min
404-1	XLIII	MgAl$_2$O$_4$ and MgO	0.4	--	257° 30 min
404-2	XLIII	TiO$_2$ and MgAl$_2$O$_4$	1	Toluene and 0.005% Monowet (MO70%)	257° 30 min
404-3	XLIII	TiO$_2$ and MgAl$_2$O$_4$	1	Toluene and 0.05% Monowet	257° 24 hrs
405-1A	XLIII	TiO$_2$ and MgAl$_2$O$_4$	0.67	0.06% Monowet	257° 30 min
405-1B	XLIII	TiO$_2$ and MgAl$_2$O$_4$	0.67	0.06% Monowet	257° 24 hrs
405-2A	XLIII	ZnO	0.67	0.06% Monowet	257° 30 min
405-2B	XLIII	ZnO	0.67	0.06% Monowet	257° 24 hrs
406-1A	XLIII	ZnS	0.67	0.06% Monowet	257° 30 min
406-1B	XLIII	ZnS	0.67	0.06% Monowet	257° 24 hrs
406-2A	XLIII	CaSiO$_3$	0.67	0.06% Monowet	257° 30 min
406-2B	XLIII	CaSiO$_3$	0.67	0.06% Monowet	257° 24 hrs
407-1	XLIII	MgO	0.67	Acetone and 0.06% Monowet	257° 30 min
407-2A	XLIII	MgO	0.44	0.07% Monowet	257° 30 min
407-2B	XLIII	MgO	0.44	0.07% Monowet	257° 24 hrs
408-1	VII	MgO	0.29	Toluene	Dried 257° 30 min, Cured 356° 1 hr
408-2	VII	MgO	0.5	Toluene	Dried 257° 30 min, Cured 356° 1 hr (each of 2 coats)
409-1A	XLIII	BN	0.4	Toluene and 0.06% Monowet	257° 30 min

Table 6 (cont.)

No. of Coating	No. of Vehicle	Pigment	Ratio of Pigment to Vehicle	Solvents or Dispersion Agents Added Before Use	Curing Conditions (°F) and Application Methods if other than Spraying
409-1B	XLIII	BN	0.4	Toluene and 0.06% Monowet	257° 24 hrs
409-2A	XLIII	BN	0.2	Toluene and 0.07% Monowet	257° 30 min
409-2B	XLIII	BN	0.2	Toluene and 0.07% Monowet	257° 30 min (rolled with glass rod)
409-2C	XLIII	BN	0.2	Toluene and 0.07% Monowet	257° 24 hrs
410-1A	XLIII	Sb_2O_3	0.67	0.06% Monowet	257° 30 min
410-1B	XLIII	Sb_2O_3	0.67	0.06% Monowet	257° 24 hrs
410-2A	XLIII	$Bi_2O_2CO_3$	0.67	0.06% Monowet	257° 30 min
410-2B	XLIII	$Bi_2O_2CO_3$	0.67	0.06% Monowet	257° 24 hrs
411-1	XXXVI (7.5% Soln.)	--	--	Methyl isobutyl ketone and acetone	R. T.
411-2	XXXVI	ZnS	0.6	Methyl isobutyl ketone and acetone	R. T.
411-3	XLIII	--	--		257° 30 min
411-4	XLIII	TiO_2	0.67		257° 30 min
412-1	XLIII (20.8) and XXXVI as 411-1 (41.7%)	ZnO^- (37.5%)	1.6	Methyl isobutyl Ketone and acetone	257° 30 min
412-2	XLIII (16.1%) and XXXVI as 411-1(32.2%)	ZnO (19.3%)	1.04	Methyl isobutyl ketone (16.2%) and acetone (16.2%)	257° 30 min
413-1	VIII	MgO	0.56	Xylene	480° 1 hr (each of two coats)
413-2	VIII	MgO	0.7	Xylene	320° 1.5 hr
413-3	VIII	ZnO	0.7	Xylene and 0.05% Monowet	75° 0.5 hr; 320° 1 hr
414-1	XLIV	ZnO	0.5	Water and 0.05% Monowet	266° 5 min
414-2	VIII	MgO	0.7	Xylene and 0.06% Monowet	320° 1 hr
414-3	XLIV	ZnO	0.33	Water and 0.045% Monowet	R. T.

Table 6 (cont.)

No. of Coating	No. of Vehicle	Pigment	Ratio of Pigment to Vehicle	Solvents or Dispersion Agents Added Before Use	Curing Conditions (°F) and Application Methods if Other than Spraying
415-1	XLV (5% soln.)	--	--	Methanol (94.5%) and Santolite MHP (arylsulfon-amide-formaldehyde, 0.5%)	230° 5 min
415-2	XLVI (2% soln.)	--	--	Acetone and 0.05% Monowet	257° 1 hr (dip-coated)
416-1	XLIII	ZnO	0.67	0.06% Monowet	R.T., then 257° 30 min
416-2	VIII	ZnO	0.67	Xylene and 0.06% Monowet	257° 4 hrs.

b. Properties of Organic Coatings

Some important properties of coatings containing organic vehicles are described in Table 7. Qualitative data about the adhesion to aluminum surfaces, the color after cure and after exposure to ultraviolet light are included. The numbers of coatings are identical to those listed in Table 6.

Although this section is concerned mainly with the adhesion problems and the color after cure, qualitative results on the stability to ultraviolet light are also given in Table 7 in order to eliminate the necessity of writing another lengthy table. Quantitative results on ultraviolet light stability will be discussed in a later section of this report.

The adhesion description of the coatings (to aluminum surface) is necessarily qualitative and arbitrary. The ratings are higher than generally accepted because surfaces were not treated or roughened to improve adhesion. Nevertheless, the following explanations should be helpful to form a more precise idea of the quality of adhesion as described in Table 7.

P = Poor -- The coating can be shaken or brushed off easily due to poor adhesion and/or cohesion, or because of flaking, peeling, and mud-cracking.

M = Moderate -- The coating does not fall off by handling or occasional shaking of the sample without touching the surface. However, the coating can be brushed off, at least partially, and it may show some flaking or cracking. Some coatings in this category may show reasonably good adhesion but poor hiding power of aluminum surfaces.

F = Fair -- The coating cannot be shaken or brushed off easily. However, it can be scratched off easily by a hard object, such as a nail, and the coating may show microscopically a rough surface, some holes and cracks. In this and higher categories of quality, the coating shows good hiding power of the aluminum surface.

G = Good -- The coating is stable to handling, touching the surface, and brushing. It shows a fairly smooth and homogeneous surface microscopically. However, parts of the coating can be removed by covering it with a Scotch tape and pulling the tape off, or the coating can be fairly easily removed by scratching it with a nail or a knife blade.

VG = Very Good -- The coating is smooth, homogeneous, adheres very well to aluminum, and cannot be removed by Scotch tape test. It is moderately difficult to remove the coating by scratching with a metal object.

E = Excellent -- The coating is smooth, homogeneous, stable to Scotch tape test and shows excellent adhesion to aluminum. The coating is very tough and resilient so that it is difficult to produce a scratch by applying a knife blade to it.

The color after the cure and thermal aging or sintering, if any, but before the exposure to ultraviolet light, is given in the third column, under Color 1.

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The next column, Color II, designates the color of those coatings which have been exposed to a fairly intensive light of an ultraviolet lamp for 5 to 8 hours at ambient conditions. If there is not discoloration from I to II, this result indicates in a qualitative way at least a moderate stability to ultraviolet light.

The color of some of the coatings which were exposed to four times the solar intensity of radiation in a vacuum is listed in the next column. The time of exposure was 18.5 hours for the coatings No. 2 to 126 and 402 to 406 (Color III) and 27 hours for the other coatings (Color III).

In the next column, the final color of coatings is indicated which were exposed to 78.5 hours of 4 times solar radiation intensity in a vacuum (Color IV), except for coatings No. 190 to 199, which were exposed to 6 suns for 124 hours (Color IV).

To save space in the table, the colors are abbreviated as follows:

w   = White, with no trace of color visible
gw = Pale greyish white; almost white.
pg = Pale grey.
g   = Grey.
dg = Dark grey.
b   = Black.
yw = Pale yellowish white; almost white.
py = Pale yellow, straw color, or light beige.
y   = Yellow.
ybr = Yellowish brown, tan.
pbr = Pale brown.
br = Brown.
pgn = Pale greenish.
gng = Greenish grey.
yg = Yellowish grey.

In the last column, a tentative selection of the organic paint vehicles has been made for continued investigation within this research program. If the properties of adhesion, cohesion, uniformity, and qualitative stability to ultraviolet light at ambient conditions appear to justify further evaluation of the paint vehicle, the coating is marked with a plus (+) in the last column of Table 7. A double plus (++) stands for coatings with good to excellent adhesive properties and relatively high stability of the vehicle and the pigment to ultraviolet light in the vacuum. A triple plus (+++) designates the most stable coating which showed negligible decrease of reflectivity after the longest time of exposure in the solar chamber.

Table 7

PROPERTIES OF ORGANIC COATINGS

No. of Coating	Adhesion	Color				Selection of Promising Coatings
		I	II	III	IV	
1	P	py				
2	M	w		y		
3	P	w				
4	P	w				
5	P	yw				
6	P	yw				
7	P	w				
8	M	w				
9	G	br				
10	VG	y		yg		
11	G	pg		br		
12	M	yw		br		
13	P	dg				
14	M	pg				
15	M	pg				
16	M	pg				
17	M	pg				
18	M	gw				
19	M	gw				
20	G	br				
21	M	gw		g		
22	F	gw				
23	F	gw				
24	F	w				
25	F	pg				
26	F	pg				
27	M	w		pg		
28	M	pbr				
29	M	gw				
30	M	w				
31	M	w		pg		
32	M	gw				
33	M	w				
34	M	w		pg		
35	M	w				
36	M	pg				
37	M	pg				
38	M	gw				
39	M	pbr				
40	M	yw		b		
41	M	pbr				
42	M	pbr				
43	M	w				
44	M	pg				
45	M	pg				
46	M	w		y		

Table 7 (Cont.)

No. of Coating	Adhesion	Color				Selection of Promising Coatings
		I	II	III	IV	
47	M	g				
48	M	g				
49	M	w				
50	M	pg				
51	E	py				
52	E	py				
53	E	py				
54	E	py				
55	F	py				
56	M	w		gw	pg	
57	M	w				
58	M	w				
59	M	w				
60	M	pbr(surface)				
61	M	pbr(surface)				
62	M	br(surface)				
63	M	ybr(surface)				
64	P	w				
65	P	yw				
66	M	w				
67	M	w		gw	pg	
68	M	w		gw		
69	E	py				
70	E	py				
71	E	py				
72	E	y				
73	E	y				
74	E	y				
75	M	w		y		
76	E	pgn				
77	E	pgn				
78	E	pgn				
79	E	pgn				
80	E	pgn				
81	E	py				
82	E	py				
83	E	py				
84	E	gng				
85	E	gng				
86	E	gng				
87	E	yg				
88	E	yg				
89	E	yg				
90	E	y				
91	E	y				
92	E	y				
93	E	py		yg		
94	E	py				
95	E	py				

Table 7 (Cont.)

No. of Coating	Adhesion	Color				Selection of Promising Coatings
		I	II	III	IV	
96	E	pgn				
97	G	pgn		yg		
98	E	yw				
99	E	yw				
100	E	yw				
101	E	yw		yg		
102	G	w				
103	G	w		yg		
104	G	w				
105	F	w				
106	F	w				
107	G	w				
108	G	w				
109	G	w				
110	G	w				
111	G	w	w			+
112	F	w				
113	G	w		gw		+
114	G	w				+
115	G	w				+
116	G	w		gw		+
117	G	w		gw		+
118	G	w		gw		+
119	G	w	yw			
120	G	w	w			+
121	F	gw		gw	pg	
122	M	gw	gw			
123	F	w				
124	F	w		gw	pg	
125	G	w		gw	Pg	+
126	G	w		gw	pg	+
127	G	w				+
128	G	yw				
129	G	w				+
130	G	w				+
131	G	w				+
132	G	w				+
133	G	w				+
134	G	w				+
135	VG	w				+
136	VG	w				+
137	VG	w				+
138	VG	w				+
139	VG	w				+
140	VG	w				+
141	VG	w				+
142	VG	pg				
143	VG	pg				

Table 7 (Cont.)

No. of Coating	Adhesion	Color				Selection of Promising Coatings
		I	II	III	IV	
144	VG	pg				
145	VG	w				+
146	VG	w				+
147	VG	w				+
148	E	w				+
149	E	w				+
150	E	w				+
151	E	w				+
152	E	w				+
153	E	w		pbr		+
154	E	w	w	br		
155	E	w	w			
156	G	yw				
157	G	yw		pbr		
158	G	yw		y		
159	G	yw				
160	G	w		y		
161	G	w				+
162	G	w				+
163	G	w				+
164	E	w	w	y		
165	E	yw	yw			
166	F	py				
167	F	pbr				
168	F	pbr				
169	P	py		y		
170	G	ygr				
171	G	ygr				
172	VG	w	py			
173	VG	w	yw			
174	VG	w	w			+
175	VG	w	w			+
176	VG	w		py		+
177	VG	w				+
178	G	w	w	y		
179	G	yw	yw	y		
180	G	w		py		+
181	G	w		w		++
182	G	w				+
183	G	w		pbr		
184	G	w				
185	G	w		pbr		
186	G	w				
187	F	w	w	gw		++
188	F	yw	yw			+

Table 7 (Cont.)

No. of Coating	Adhesion	Color I	II	III	IV	Selection of Promising Coatings
189	G	w	w	w		++
190	G	yw	w		w	++
191	G	yw	w	w		++
192	G	w	w	w		++
193	G	w	w		w	++
194	G	w	w	w		++
195	G	w	w		w	++
196	G	w	w	w		++
197	G	w	w	w		++
198	G	w			w	+++
199	G	w			w	++
401-1	G	py				
401-2	G	py				
401-3	G	w				
401-4	G	ybr				
401-5	G	w				
401-6	F	g				
402-1	G	yw				
402-2	G	yw				
402-3	VG	yw	py	y		
402-4	VG	yw				
402-5	E	py	py			
402-6	E	py	py			
403-1	E	yw		yw		+
403-2	E	w	yw			
404-1	F	w				
404-2	G	w	gw			
404-3	G	w				
405-1A	VG	w	yw			
405-1B	VG	yw				
405-2A	E	w	yw	py		+
405-2B	E	yw	yw	py		+
406-1A	E	w	yw	py		
406-1B	E	w	yw	py		
406-2A	G	pg				
406-2B	G	pg				
407-1	P	w				
407-2A	F	w		g		
407-2B	F	py				
408-1	G	gw				+
408-2	VG	pg				+
409-1A	F	w				
409-1B	F	gw				
409-2A	F	gw				
409-2B	G	gw		y		
409-2C	F	pg				
410-1A	VG	w		pg		
410-1B	VG	y				

Table 7 (Cont.)

No. of Coating	Adhesion	Color				Selection of Promising Coating
		I	II	III	IV	
410-2A	G	w		g		
410-2B	G	gw				
411-1	F	w				
411-2	P	w				
411-3	G	w				
411-4	G	w				
412-1	P	w				
412-2	F	pg				
413-1	G	w				
413-2	VG	w		y		
413-3	E	w		gw		+
414-1	F	gw				
414-2	E	w		y		
414-3	P	gw				
415-1	G	gw				
415-2	F	gw				
416-1	E	w		gw		++
416-2	E	w		gw		+

c. Selection of Organic Coating Vehicles with Good
to Excellent Properties of Adhesion

The problems of adhesion will be discussed in this section, while the color changes caused by ultraviolet light, shown in Table 7, will be discussed in a later section of this report.

As pointed out before, when poor to excellent adhesion was described or approximately defined, the qualification of adhesion in Table 7 does not include only the adhesivity of the coating to aluminum but also some other mechanical properties. A coating with good to excellent adhesion also shows good cohesion, does not peel readily, does not form cracks or pinholes, has a smooth texture when seen in a microscope under moderate magnification, has a good hiding power of the aluminum surface, cannot be brushed off, and cannot be easily removed by scraping.

In the chemical class of semi-inorganic resins with organic "framing" groups, the following paint vehicles showed good to excellent adhesion:

RTV-11 Silicone Liquid Paste (IV)
LTV-602 Silicone Liquid (V)
SE55 IN Silicone Gum (VI)
840 Silicone Resin (VII)
806A Silicone Resin (VIII)

The other paint vehicles of this group were eliminated because of poor adhesion (I), discoloration and peeling (III), and discoloration upon heating to 300°F or by ultraviolet light (II). Although higher-molecular-weight and more pure polytitanoxane resins (II), especially with methyl "framing" groups, may prove to be more stable to heat and ultraviolet light, yet their stability is not expected to match that of silicones. There is an analogy with the corresponding inorganic compounds: titania is less stable to ultraviolet light than silica.

From the class of aliphatic fluorine-containing resins, the following coating vehicles were found to have good to excellent adhesion and other concurrent mechanical properties:

800 Kel-F Copolymer (XVI)
8213 Kel-F Coating Latex, modified (XVIII)
L 18 Kynar (XXII)
461 Exon (XXIII)
Viton A and B, of which the best was the clear solution of B (XXVII)
A mixture of Teflon Powder No. 7 (IX) and of 800 Kel-F (XVI) such
    as in coatings No. 148 to 153.

In spite of numerous coatings prepared and several approaches of curing and paint application tried, it was established that pigmented coatings based on Teflon (IX through XIV) had only fair adhesion in most favorable cases. This conclusion is valid if no other paint vehicles are mixed with Teflon modifications, and if the upper limit of curing temperature (300°F) is observed.

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The use of high-molecular-weight polytrifluorochloroethylene with (XX) or without (XV) phosphonic acid groups appears to be promising, if 1,1,2, 2-tetrachloro-3,3,4,4-tetrafluorocyclobutane is used as solvent, together with some toluene or xylene. These resins form a strong and colorless film on an aluminum surface. However, the compounding problem with pigments, in particular zinc oxide, and the application technique should be further improved.

The following were the major observed drawbacks of other fluorinated paint vehicles: XVII, mud-cracking; XIX, yellowing; XXI, discoloration; XXIV, XXV, and XXVI, more rapid discoloration by heat or radiation than that of the stable modification XXVII.

The following organic polyester coatings showed excellent adhesion to aluminum; XXXI, XXXII, XXXIII, XXXIV, and XXXV. However, the disadvantage of all these pigmented coatings was their color, ranging from pale yellow to darker shades. The drawbacks of other ester type vehicles were: XXVII, rapid evaporation during the thermal cure; XXIX, granular surface and poor hiding power of aluminum at the applied concentration of the pigment; XXX, discoloration upon rapid thermal cure; XXXVI, poor adhesion to aluminum, which was somewhat improved in mixtures with XLIII (Coating 412-2). However, in the latter case, the coating had a greyish color.

Among the epoxy resins studied, 159 Kopoxite (XXXVII) showed good adhesion to aluminum, and the coatings were white. Other epoxy resins (XXXVIII, XXXIX, and XL) were investigated merely as substrates or primary layers for ceramic coatings. Obviously, among conventional epoxies and polyesters, a very high radiation stability could not be expected.

The miscellaneous organic paint vehicles and primers (XLI through XLVI) were applied to aluminum specimens as a prime coat and then forwarded to the Ceramics Division for subsequent inorganic top coating. The only paint vehicle of this class which was investigated independently for organic top coatings, was Leonite 201-S (XLIII). Leonite coatings containing zinc oxide, zinc sulfide, or some other pigments were very white, smooth, homogeneous, and showed good to excellent adhesion to aluminum surfaces. Leonite 201-S is classified among miscellaneous vehicles since its silicone and epoxy content is apparently minor compared to the acrylic resin structure, and since the exact chemical composition has not been disclosed by the manufacturer.

V. RESULTS OF SOLAR EXPOSURES

Various inorganic pigments, vehicles and paints were subjected to solar simulation in three different tests: 1.5 suns for 50 hours, 4 suns for 60 hours and 4 suns for 67 hours. For ease of reference, the runs will be designated Test A, Test B, and Test C, respectively. Organic coatings were included in Test B (60 hr), but they were given an additional overnight run of 18.5 hours at 4 suns along with new organic materials. A separate run of 27 hours at 4 suns was also made with organics. The 18.5, 60 + 18.5 or 78.5 and the 27 hour tests are designated D, E, and F, respectively.

A. Inorganic Pigments and Vehicles

A variety of white powders were exposed to the relatively moderate conditions of Test A. Included in this test as powders were the three prime vehicle candidates. Selected reflectivity measurements in the visible range before and after exposure are tabulated in Table 8.

The data confirmed the visual observation that the lead and antimony materials all discolored badly. Of the zirconium compounds, zircon appeared more promising than the oxide, although the latter was whiter initially. Wollastonite (calcium silicate) and silica showed reflectivity changes comparable to that for zircon. With the exception of zinc compounds, the other materials all experienced considerable degradation. Reflectivities of zinc oxide and sulfide remained virtually unchanged.

Among the possible vehicles, potassium silicate revealed the least change, both visibly and in the actual optical measurements. Ludox, a colloidal silica, discolored badly; this, coupled with its physical fragility, eliminated its further consideration.

The results of the first exposure test indicated a superiority of natural mined minerals over synthetic laboratory chemicals (with the exception of zinc compounds) as pigments. Thus Test B included several mineral products which, although of low refractive indices and initial reflectivities, might possess the required space stability. Dicalite (diatomaceous earth) and Molochite (a calcined china clay) were the least degraded of the pigments in this run as shown in Table 9.

Under the more severe conditions of Test B, zirconium silicate degraded rather severely. A comparison between the TAM milled of Test A and Superpax or Superpax "A" of Test B shows that reflectivity losses in per cent were approximately three times as great for the latter zircons. The whiteness of Superpax "A" was slightly improved upon hydrochloric acid leaching; however, no retardation in color degradation was realized by this treatment. The other minerals experienced changes comparable to those of zircon.

Considerable color degradation occurred for most of the "synthetic" chemicals. Reflectivity losses were generally greater than for the minerals. One exception was calcined La_2O_3 which fared about as well as zircon; however, its strong hygroscopicity may limit its usefulness. The metastable materials, gamma alumina in Test A and cubic (non-stabilized) ZrO_2 in Test B, degraded much more severely than their stable counterparts, alpha Al_2O_3 and monoclinic ZrO_2.

Also included in Test B were several other pigment candidates contained in aluminum dishes as loose powders. Moderate color changes were observed for the following: a high potash feldspar, cristobalite, lithium zirconium silicate and enstatite (No. 140 Alabama talc calcined at 1200°C for two hours in nitrogen). Stronger discoloration was exhibited by lithium titanate and monocalcium phosphate. Both potassium silicate and aluminum phosphate vehicle samples, previously exposed in Test A, underwent considerable discoloration with the added exposure.

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The screening programs of Tests A and B disclosed the superior solar stability of zinc oxide and sulfide. Both of these pigment samples, previously irradiated in Test A, received further exposure along with some new pigments in Test C. The results of this test are tabulated in Table 10.

Zinc oxide powders of lower purities from different suppliers, AZO ZZZ-66 (99.80%) from American Zinc Sales and USP grade from Allied Chemical, showed extremely small reflectivity losses, comparable to that for SP 500 from New Jersey Zinc. The previously exposed S.P 500 sample degraded slightly in this run, mainly in the vicinity of 440 millimicrons. A similar but slightly greater loss resulted for the zinc sulfide powder.

Considerable degradation occurred in the other pigment specimens. However, the reflectivity loss for Ajax SC (calcined kaolin) was significantly less than that for Ajax P, the uncalcined form (Test B, Table 9).

Pigment studies to date have shown the clear superiority of zinc oxide for solar stability, and a second possible material, zinc sulfide. Two other materials which appear of interest are diatomaceous earth and Molochite, a mixture of mullite and amorphous silica. Although ZnO appears to be the logical choice, its relative thermal instability indicates the desirability of continued search for other compounds as backup materials. Table 11 contains more detailed information on two pigments.

Reflectivity losses in the visible range of various pigments are graphically illustrated in Figures 7 through 12 with increasing color degradation. Figure 13 depicts the superiority of a calcined material over its hydrated counterpart. In general changes are greatest in the near-UV and decrease with higher wavelengths.

B. Inorganic Paints

The first space environment run, Test A, included paints utilizing a variety of binders (see Table 12). The potassium silicate paints fared moderately well under space simulation. Although reflectivities of the paints were initially lower than for the corresponding pigments alone, losses due to solar exposure were quite small, indicating a possible protective property of the silicate. One exception to this phenomenon was the spinel-silicate composition which degraded considerably compared to the other paints. The zinc oxide paint clearly showed its superiority, similar to its behavior among pigments. The phosphate-bonded zirconia paints also experienced relatively small changes on space exposure. On the other hand, Ludox paints yellowed noticeably and this was reflected in the optical measurements. The zinc sulfide-silicone paints furnished by Jet Propulsion Laboratory revealed very little change in reflectivity.

The shortcomings of colloidal silica and monoaluminum dihydrogen phosphate as binders, i.e., poor solar stability and need for a primer coat respectively, suggested emphasis on potassium silicate. A highly pure form marketed by Sylvania Electric Products has been used almost exclusively in the later solar stability tests. The particulars on this binder are:

PS7   specific gravity   = 1.330

total solids   = 35.00%

Fe   = .0025%

Cu   = 4×10^{-6}%

mol ratio   = $1\ K_2O : 3.31\ SiO_2$

Continued exposure of the zinc oxide paint (sample No. 1-9-5) in Test B resulted in extremely small reflectivity losses as tabulated in Table 13. Paints incorporating lanthana, alumina trihydrate and Wollastonite all experienced marked color changes; losses for zirconia-containing compositions were noticeably less. The superior optical stability of paints as compared to the pigment alone revealed in Test A was substantiated only by the zirconia paints in Test B. However, the presence of chemically and/or mechanically combined water in uncalcined La_2O_3 and $Al_2O_3 \cdot 3H_2O$ may have contributed to possible degradation through volatilization in a high vacuum.

Particular emphasis was placed on silicate-bonded zinc oxide paints in Test C based on earlier performance. All formulations in Test C were mixed by agitation with porcelain balls for about five minutes. Absorbtivity (α) and emissivity (ϵ) measurements as well as reflectivity losses appear in Table 14.

Among the non-zinc paints, an enstatite-potassium silicate formulation experienced the strongest discoloration. Similar reflectivity losses of a lesser extent were observed for the other paints. Least degraded was silicate-bonded Molochite No. 6 (mullite + amorphous silica). The influence of water spotting on some of the samples (see footnote 4, Table 13) on the optical measurements is not known. A re-run of the formulations in question appears advisable.

All zinc oxide-potassium silicate paints experienced only very small reflectivity losses, mainly in the 440 millimicron region. Determination of α values shows correspondingly small changes. Rather high ϵ values were obtained for four different ZnO-silicate samples, all in excess of 0.90. If an emissivity of 0.90 might be assumed for sample 1-9-5, the α / ϵ ratio of this sample which has received about 580 sun hours is 0.17, well below the maximum desirable limit. When the pigment/binder ratio is lowered to 2.15:1 (sample 2-10-7a) α increases to 0.26, almost double that of the higher pigment containing samples. The desirability of a high pigment to vehicle ratio is well emphasized by these figures.

A zinc sulfide-silicate paint discolored slightly more than ZnO-silicate, but the degradation was considerably less than for any of the other paints which have been studied. Two JPL silicone-ZnS paints, P283 and P260, previously exposed to about 75 sun hours, revealed considerable degradation after the additional exposure of Test C.

Degradation of various selected paints in the visible range are graphically presented in Figures 14a to 18a. Figures 14b to 18b show reflectivity losses over a wider range for α determinations.

C. Organic Paints and Vehicles

Qualitative results on color changes of organic coatings caused by ultra-violet light at ambient conditions as well as by simulated solar exposures in vacuum have been included in Table 7 of the preceding section on Preparation of Materials.

Quantitative results concerning the changes of reflectivity of organic paints in the visible spectrum due to simulated solar exposures are given in Table 15 and in the remaining plots. This table does not include all organic coatings prepared and irradiated. In the early part of the screening program, some organic coatings discolored drastically in the solar chamber, and only their qualitative color changes are given in this report (Table 7).

Table 8

CHANGES IN REFLECTIVITY FOR PIGMENTS AND VEHICLES DUE TO SOLAR SIMULATION, TEST A

Sample	Material	Supplier		Reflectivity, 1 % at.			
				380 mμ	440 mμ	600 mμ	700 mμ
A	Sb_2O_3	National Lead	(a)[2]	80.0	92.5	96.5	97.0
			(b)[3]	32.0	36.5	50.0	59.5
B	Basic silicate white lead 45X	National Lead	(a)	75.0	88.5	91.5	92.0
			(b)	54.0	66.5	82.5	87.5
C	Basic carbonate white lead	National Lead	(a)	89.0	93.5	96.0	96.5
			(b)	39.0	52.0	80.5	87.5
D	H.P. ZrO_2 [4]	Titanium Alloy Manufacturing Div.	(a)	76.5	92.5	97.0	97.0
			(b)	49.5	65.5	90.5	93.5
H	C.P. ZrO_2	Fairmount	(a)	80.0	89.0	95.0	95.5
			(b)	53.5	68.0	90.0	93.5
N	H.P. ZrO_2 No. 2 [4]	TAM	(a)	80.0	94.0	96.5	96.0
			(b)	50.0	65.5	89.0	92.5
M	C.P. ZrO_2 No. 2	TAM	(a)	90.5	96.0	97.5	97.0
			(b)	64.0	75.5	92.5	95.0
E	Milled zircon $ZrSiO_4$	TAM	(a)	78.0	87.0	93.5	94.5
			(b)	68.5	80.0	91.0	93.5
L	Ultrox 1000W $ZrSiO_4$	Metal-Thermit	(a)	76.5	86.0	93.5	94.5
			(b)	64.5	78.0	90.5	93.0
F	S.P. 500 ZnO	New Jersey Zinc	(a)	30.0	95.0	99.0	98.5
			(b)	30.0	95.0	99.0	99.0
K	ZnS, reagent grade	Matheson, Coleman and Bell	(a)	66.0	91.0	94.5	70.5
			(b)	64.5	89.0	94.0	70.5
O	Synthetic $CaSiO_3$	Johns-Manville	(a)	81.0	86.0	90.0	90.5
			(b)	40.0	58.0	81.0	85.0
P	Wollastonite, $CaSiO_3$	Cabot	(a)	90.0	92.5	94.5	94.0
			(b)	72.0	81.0	91.5	92.5

Table 8 (cont'd.)

CHANGES IN REFLECTIVITY FOR PIGMENTS AND VEHICLES DUE TO SOLAR SIMULATION, TEST A

Sample	Material	Supplier		Reflectivity, 1 % at.			
				380 mμ	440 mμ	600 mμ	700 mμ
I	Ottawa Special SiO₂	Ottawa Silica Co.	(a)	85.0	88.5	92.5	93.0
			(b)	66.0	77.5	90.0	92.0
S	Alucer MA Al₂O₃	Gulton Industries	(a)	91.0	93.5	90.0	86.5
			(b)	25.0	49.5	82.5	83.5
T	MgO, reagent grade	Mallinckrodt	(a)	99.0	98.5	98.5	98.5
			(b)	56.5	71.0	92.5	96.0
V	BN	Carborundum	(a)	85.5	88.0	92.5	92.5
			(b)	54.5	65.0	84.0	87.5
R	Spinel, MgAl₂O₄	Linde	(a)	95.5	97.5	97.0	96.5
			(b)	53.0	70.0	92.5	95.0
	Titanox TG	TAM					
	SrTiO₃	TAM					
Binders:							
W	PS7, potassium silicate	Sylvania	(a)	92.5	94.0	96.0	96.5
			(b)	82.0	88.5	94.5	95.5
X	aluminum phosphate	Victor Chemical	(a)	94.5	95.5	96.0	96.0
			(b)	66.5	74.5	84.5	88.0
	Ludox, colloidal silica	DuPont					

These powders were not compactable, so they were placed in the space chamber in aluminum dishes as loose powders. Discoloration to a gray may be termed "slight" for SrTiO₃ and "heavy" for TiO₂

Treated in same manner as TiO₂ and SrTiO₃ above. Definite yellow discoloration.

1. Reflectivity based on MgO scale. Wavelengths chosen arbitrarily in visible range.
2. Reflectivity prior to space environment exposure.
3. Reflectivity after space environment exposure.
4. Different lots of same material. Both lots contained carbonaceous material as small black specks.

Table 9

CHANGES IN REFLECTIVITY FOR PIGMENTS AND VEHICLES DUE TO SOLAR SIMULATION, TEST B

Sample	Material	Supplier		Reflectivity,[1] % at.			
				380 mμ	440 mμ	600 mμ	700 mμ
Mineral Products:							
a	C.P. zircon (ZrSiO$_4$)	Titanium Zirconium Co.	(a)[2]	68.0	75.5	84.0	86.5
			(b)[3]	44.0	55.5	71.5	79.0
c	Superpax zircon	TAM	(a)	80.5	86.5	92.5	93.5
			(b)	52.0	65.0	84.5	87.5
d	Superpax "A" zircon	TAM	(a)	79.5	85.5	90.5	91.5
			(b)	50.0	64.0	82.5	86.5
o	Superpax "A" zircon (HCl leached)	TAM	(a)	83.0	89.0	92.5	93.0
			(b)	44.0	57.0	75.5	81.0
g	Dicalite WB-5, diatomaceous earth	Great Lakes Carbon Co.	(a)	87.5	92.0	93.5	93.5
			(b)	80.0	87.5	93.0	93.0
h	No. 140 Alabama talc, MgSiO$_3$·n H$_2$O	Whittaker, Clark and Daniels	(a)	85.0	89.0	92.0	93.0
			(b)	54.0	62.0	73.5	76.0
l	Wollastonite C-6, CaSiO$_3$	Cabot	(a)	90.5	92.0	93.5	93.0
			(b)	58.5	70.0	86.5	88.5
r	Calcite, CaCO$_3$	Whittaker, Clark and Daniels	(a)	85.0	89.0	93.5	94.0
			(b)	57.0	70.5	89.5	91.5
t	Ajax P kaolin	Georgia Kaolin	(a)	61.0	73.0	84.5	86.0
			(b)	37.0	46.5	60.0	66.0
v	Superfine Molochite, 3Al$_2$O$_3$·2SiO$_2$ + SiO$_2$	Paper Makers Importing Co.	(a)	80.5	84.5	86.5	86.0
			(b)	66.5	75.5	84.5	84.5
Synthetic Materials:							
e	C.P. ZrO$_2$	Titanium Zirconium Co.	(a)	78.0	88.0	90.5	91.0
			(b)	53.5	65.5	80.0	82.5
f	CMC-6-CP ZrO$_2$	Carborundum	(a)	85.5	93.5	97.0	97.5
			(b)	36.5	49.0	72.5	77.5

Table 9 (cont'd.)

CHANGES IN REFLECTIVITY FOR PIGMENTS AND VEHICLES DUE TO SOLAR SIMULATION, TEST B

Sample	Material	Supplier		Reflectivity,[1] % at.			
				380 mμ	440 mμ	600 mμ	700 mμ
i	Alucer MC Al$_2$O$_3$ (alpha)	Gulton Industries	(a)	100	100	100	100
			(b)	62.0	74.0	91.5	93.5
m	Aluminum meta-phosphate	Victor Chemical	(a)	97.0	97.5	96.5	96.0
			(b)	50.0	61.5	80.0	83.5
n	Potassium meta-phosphate	Victor Chemical	(a)	97.0	99.5	99.0	98.5
			(b)	52.0	65.0	87.5	90.5
p	La$_2$O$_3$ (1000°C/16 hours)	Lindsay Chemical	(a)	87.0	89.0	94.5	97.0
			(b)	62.5	73.0	90.5	94.5
s	Cubic ZrO$_2$	TAM	(a)	73.0	88.0	95.5	93.5
			(b)	18.0	33.0	73.5	83.5
Vehicles:							
W	PS7, potassium silicate	Sylvania	(a)	92.5	94.0	96.0	96.5
			(b$_1$)[4]	84.5	88.5	94.5	95.5
			(b$_2$)[5]	49.0	62.5	86.5	91.5
X	Aluminum phosphate	Victor Chemical	(a)	94.5	95.5	96.0	96.0
			(b$_1$)	68.5	74.0	86.0	86.0
			(b$_2$)	46.5	55.0	71.0	75.0

1. Reflectivity based on MgO scale. Wavelengths chosen arbitrarily in visible range.
2. Reflectivity prior to space environment exposure.
3. Reflectivity after space environment exposure.
4. Reflectivity after space environment exposure, Test A.
5. Reflectivity after two space environment exposures, Test A and Test B.

Table 10

CHANGES IN REFLECTIVITY FOR PIGMENTS DUE TO SOLAR SIMULATION, TEST C

Sample	Material	Supplier		Reflectivity,[1] % at.			
				380 mµ	440 mµ	600 mµ	700 mµ
F	S.P. 500 ZnO	New Jersey Zinc	(a)[2]	30.0	95.0	99.0	98.5
			(b₁)[4]	30.0	95.0	99.0	99.0
			(b₂)[5]	31.5	91.0	97.5	97.5
(4)	AZO-ZZZ 66 ZnO	American Zinc Sales	(a)[2]	31.5	93.0	99.0	99.0
			(b)[3]	31.5	91.0	98.0	98.0
(5)	U.S.P. ZnO	Allied Chemical	(a)	30.0	93.0	98.5	98.0
			(b)	35.0	91.5	97.5	98.0
K	Reagent grade ZnS	Matheson, Coleman and Bell	(a)	66.0	91.0	94.5	70.5
			(b₁)	64.5	89.0	94.0	70.5
			(b₂)	62.5	81.0	91.5	69.5
(6)	Ajax SC, calcined kaolin	Georgia Kaolin	(a)	68.0	78.0	87.0	88.5
			(b)	50.5	65.0	81.0	84.0
(9)	Mullite 3Al₂O₃·2SiO₂	Carborundum	(a)	88.0	90.0	91.0	91.0
			(b)	56.5	69.0	86.5	88.5
(10)	No. 7900 Vycor	Corning Glass	(a)	92.0	94.0	95.0	97.0
			(b)	41.0	43.0	44.5	45.5
(13)	Reagent grade BaCO₃	Allied Chemical	(a)	96.0	98.5	99.0	99.0
			(b)	58.5	71.0	93.5	96.0
(14)	Magnesium trisilicate U.S.P.	Mallinckrodt	(a)	96.0	97.5	99.0	99.0
			(b)	11.0	18.5	44.5	58.5
(15)	Reagent grade CaF₂	Allied Chemical	(a)	93.0	94.5	97.0	97.0
			(b)	47.5	61.0	87.5	92.0

1. Reflectivity based on α-Al₂O₃ scale. Wavelengths chosen arbitrarily in visible range.
2. Reflectivity prior to space environment exposure.
3. Reflectivity after space environment exposure.
4. Reflectivity after space environment exposure, Test A.
5. Reflectivity after space environment exposure, Test A and Test C.

Table 11

PIGMENTS FOR WHITE COATINGS

Horse Head S. P. ZnO 500,
New Jersey Zinc Company

Analysis:

Fe	-	.0001%	Al	-	< .001%
Cu	-	< .0001%	Ca	-	< .001%
Mn	-	.0001%	Na	-	.0003%
PbO	-	.0008%	Si	-	< .0003%
As_2O_3	-	.00001%	Mg	-	< .0004%
CdO	-	.0005%			

Insoluble in HCl	-	< .001%
SO_3 (total S as)	-	.004%
H_2O soluble salts	-	.06%
Loss at 110°C	-	, 10%

Specific Surface	-	3. 0-4. 3 m^2/g
Surface Mean Diameter		.25-.35 microns

Dicalite WB5,
Great Lakes Carbon Co.

Analysis:

SiO_2	-	94.57%	CaO	-	0.10%
Na_2O	-	2.35%	MgO	-	0.25%
Al_2O_3	-	1.70%	TiO_2	-	0.07%
Fe_2O_3	-	0.90%	V_2O_5	-	0.05%

Ignition loss	-	0.01

Surface area	-	2. 1 m^2/g		
Average size,	-	+40 μ	-	0.5%
		20-40 μ	-	1.0%
		10-20 μ	-	6.5%
		6-10 μ	-	8.0%
		3-6 μ	-	40.0%
		-3 μ	-	44.0%

Table 12

CHANGES IN REFLECTIVITY FOR PAINTS DUE TO SOLAR SIMULATION, TEST A

Sample	Composition[1]		Reflectivity, 3, % at.			
			380 $m\mu$	440 $m\mu$	600 $m\mu$	700 $m\mu$
AM	20g C.P. ZrO_2 10 cc Ludox AM (alumina modified)	(a)[4] (b)[5]	74.5 43.0	88.0 61.5	95.5 88.0	96.5 92.0
HS	20g C.P. ZrO_2 10cc Ludox HS[2]	(a) (b)	78.5 46.5	91.0 64.5	96.5 90.0	96.5 93.0
NH_3	20g C.P. ZrO_2 10cc Ludox (ammonia stabilized)	(a) (b)	75.0 43.0	86.5 63.0	95.5 88.5	96.0 92.5
1-5-4	30g H.P. ZrO_2 15cc PS7, potassium silicate 5cc H_2O	(a) (b)	66.5 61.5	86.0 79.5	90.5 87.5	89.5 87.5
1-9-2	30g H.P. ZrO_2 15cc PS7 5cc H_2O	(a) (b)	70.0 65.0	88.5 83.0	94.0 91.5	93.0 91.5
1-9-4	30g $ZrSiO_4$, milled 15cc PS7 5cc H_2O	(a) (b)	60.5 57.0	75.5 70.5	83.5 80.5	84.0 82.5
1-9-5	20g ZnO S.P. 500 10cc PS7 20cc H_2O	(a) (b)	31.0 31.0	96.0 95.5	98.0 98.0	97.5 97.0
1-16-6	30g C.P. ZrO_2 15cc PS7 5cc H_2O	(a) (b)	77.0 74.0	89.0 83.5	92.0 90.5	92.0 91.5
1-19-2[2]	30g C.P. ZrO_2 15cc $Al(H_2PO_4)_3$ (50%) 5cc H_2O	(a) (b)	67.5 62.0	76.0 71.5	86.0 85.0	89.0 88.5
1-12-4	10g $MgAl_2O_4$ 15cc PS7 15cc H_2O	(a) (b)	88.5 62.5	93.5 76.0	98.0 94.5	98.0 96.0

Table 12 cont'd.)

CHANGES IN REFLECTIVITY FOR PAINTS DUE TO SOLAR SIMULATION, TEST A

Sample	Composition[1]		Reflectivity, [3] % at.			
			380 mμ	440 mμ	600 mμ	700 mμ
P 258	Silicone-zinc sulfide samples furnished by Jet Propulsion Laboratory	(a)	60.0	85.0	89.0	62.0
		(b)	52.0	78.5	88.5	62.0
P 260		(a)	60.0	85.0	91.0	62.5
		(b)	51.0	79.0	90.0	62.5
P 283		(a)	64.0	87.5	93.0	69.5
		(b)	58.0	83.5	92.0	69.5
P 284		(a)	65.0	88.0	93.0	69.5
		(b)	58.0	84.0	92.5	69.5

1. See Table I for suppliers.
2. Painted on acrylic coated aluminum.
3. Reflectivity based on MgO scale. Wavelengths chosen arbitrarily in visible range.
4. Reflectivity prior to space environment exposure.
5. Reflectivity after space environment exposure.

Note: Paints were sprayed on 1 x 3-inch type 6061 aluminum pieces with an air brush. All samples were air dried for 18 hours and cured at 130-135°C for 24 hours.

Pigment/binder ratios:　　Ludox, 5.33:1
　　　　　　　　　　　　Potassium silicate, 4.30:1
　　　　　　　　　　　　Aluminum phosphate, 2.80:1

Table 13

CHANGES IN REFLECTIVITY FOR PAINTS DUE TO SOLAR SIMULATION, TEST B

Sample	Composition		Reflectivity,[1] % at.			
			380 mμ	440 mμ	600 mμ	700 mμ
1-23-0[6]	10g H.P. ZrO$_2$ (TAM) 5cc PS7 potassium silicate (Sylvania) 2cc H$_2$O	(a)[2] (b)[3]	67.5 52.0	82.5 67.0	84.5 79.5	82.5 80.5
1-25-0[6]	20g C.P. ZrO$_2$ (TAM) 10cc aluminum phosphate (Victor) 4cc H$_2$O	(a) (b)	81.5 64.0	88.5 72.0	90.5 83.5	90.5 85.5
2-4-3	20g CaSiO$_3$, P-1 Wollastonite (Cabot) 10cc PS7 6cc H$_2$O	(a) (b)	74.5 41.5	78.5 52.5	83.5 71.5	83.5 77.5
2-5-3	20g Al$_2$O$_3$·3H$_2$O, C-35 (Alcoa) 10cc PS7[3] 4cc H$_2$O	(a) (b)	77.5 48.0	79.5 58.5	80.5 74.0	80.0 77.0
2-5-4	10g La$_2$O$_3$ (Lindsay) 5cc PS7 5cc H$_2$O	(a) (b)	89.5 45.0	92.5 54.0	95.0 77.5	94.5 85.5
1-9-5	20g ZnO, S.P. 500 (New Jersey Zinc) 10cc PS7 20cc H$_2$O	(a)[4] (b$_1$)[5] (b$_2$)	31.0 31.0 31.0	96.0 95.5 94.5	98.0 98.0 97.5	97.5 97.0 97.0

1. Reflectivity based on MgO scales. Wavelengths chosen arbitrarily in visible range.
2. Reflectivity prior to space environment exposure.
3. Reflectivity after space environment exposure.
4. Reflectivity after space environment exposure, Test A.
5. Reflectivity after two space environment exposures, Test A and Test B.
6. The zirconia paints were applied on Leonite (silicone-epoxy modified acrylic)-coated aluminum.

Note: Paints were sprayed on 1 x 3-inch type 6061 aluminum plates with an air brush. All samples were air dried for 18 hours and cured at 125-135°C for 24 hours. Pigment/binder ratio for all silicate paints is 4.3:1, and 2.8:1 for the phosphate formulation.

Table 14

CHANGES IN REFLECTIVITY FOR PAINTS DUE TO SOLAR SIMULATION, TEST C

Sample	Composition	Remarks		Reflectivity[1], % at.				
				380 mμ	440 mμ	600 mμ	700 mμ	α
1x3":								
1-9-5	20g ZnO, SP 500 10cc PS7 20cc H$_2$O	After Test A → After Tests A + B → After Tests A + B + C →	(a) (b$_1$) (b$_3$) (b$_4$)	31.0 31.0 31.0 30.5	96.0 95.5 94.5 91.0	98.0 98.0 97.5 96.0	97.5 97.0 97.0 96.0	 0.154
2-13-0b	30g ZnO, SP 500 15cc PS7 30cc H$_2$O		(a)[2] (b)[3]	30.5 32.5	95.0 92.5	97.5 96.5	97.0 96.0	0.149 0.156
2-12-3b	2g ZnO, SP 500 1cc PS7 1cc H$_2$O	Brush painted	(a) (b)	29.5 28.5	94.0 91.5	96.5 95.5	95.5 95.5	0.164 0.177
2-10-7	20g ZnO, SP 500 20cc PS7 10cc H$_2$O	Pigment:binder = 2.15:1	(a) (b)	22.5 20.5	87.5 84.5	86.5 85.5	84.5 83.5	
2-10-0	15g ZnS 10cc PS7 5cc H$_2$O	Pigment:binder = 3.22:1	(a) (b)	63.5 60.5	85.0 81.0	90.5 88.5	67.5 67.0	0.220 0.231
2-11-3[4]	10g CP ZrO$_2$ 5cc PS7 2.5cc H$_2$O		(a) (b)	82.5 62.5	90.5 73.5	93.0 87.0	92.5 89.5	0.140 0.205
2-11-4[4]	15g CP ZrO$_2$ 7.5cc AP6 4cc H$_2$O	Sprayed on Leonite organic primer. Pigment:binder = 2.80:1	(a) (b)	79.5 63.5	84.5 70.5	87.5 81.0	87.5 83.5	0.156 0.267
2-12-4	15g CP ZrO$_2$ 7.5 cc N-silicate[5] 4cc H$_2$O	Pigment:binder = 3.83:1	(a) (b)	82.5 67.5	90.5 77.0	92.5 87.5	92.5 89.5	0.150 0.192

Table 14 (cont'd.)

CHANGES IN REFLECTIVITY FOR PAINTS DUE TO SOLAR SIMULATION, TEST C

Sample	Composition	Remarks		Reflectivity[1], % at.				α
				380 mμ	440 mμ	600 mμ	700 mμ	
2-10-3	5g Dicalite WB5 / 10cc PS7 / 10cc H$_2$O	Pigment:binder = 1.07:1	(a)	79.5	84.5	88.5	88.0	0.186
			(b)	60.5	71.5	83.5	85.5	0.229
2-11-0	20g Glassrock / 10cc PS7 / 5cc H$_2$O	(fused silica)	(a)	68.5	71.5	76.0	76.5	0.295
			(b)	52.5	60.5	72.0	74.5	0.329
2-13-3	15g Superpax / 7.5cc PS7 / 7.5 cc H$_2$O	(zircon)	(a)	69.0	79.0	88.5	89.0	0.180
			(b)	52.5	63.0	81.5	86.0	0.249
2-13-5	15g C-35 / 7.5cc PS7 / 4cc H$_2$O	(Al$_2$O$_3$·3H$_2$O)	(a)	73.5	75.5	75.5	75.5	0.345
			(b)	55.5	64.5	72.5	73.5	0.371
2-12-0[4]	2g Enstatite / 1cc PS7 / 1cc H$_2$O	Talc, 1200°C/2 hr/N$_2$ Brush painted	(a)	89.5	92.5	94.5	94.5	0.130
			(b)	56.5	66.5	84.0	88.5	0.219
2-9-4[4]	15g Molochite SF / 7.5cc PS7 / 7.5cc H$_2$O	(mullite + amorphous silica)	(a)	69.5	75.5	81.5	81.5	0.252
			(b)	50.5	60.5	75.5	77.5	0.326
2-10-5[4]	20g Molochite #2 / 10cc PS7 / 5cc H$_2$O		(a)	61.0	74.5	82.5	82.5	
			(b)	54.5	68.5	79.5	80.5	
2-10-6[4]	30g Molochite #6 / 15cc PS7 / 7.5cc H$_2$O		(a)	65.5	74.5	82.5	82.5	
			(b)	57.5	68.0	79.0	80.5	
2x2" (JPL):								
P 283	ZnS-silicone	After Test A →	(a)	64.0	87.5	93.0	69.5	0.196
		After Tests A + C →	(b$_1$)	58.0	83.5	92.0	69.5	0.204
			(b$_2$)	46.5	70.5	89.5	68.0	0.248

Table 14 (cont'd.)

CHANGES IN REFLECTIVITY FOR PAINTS DUE TO SOLAR SIMULATION, TEST C

Sample	Composition	Remarks		Reflectivity[1], % at.				α	ϵ
				380 mμ	440 mμ	600 mμ	700 mμ		
P260	ZnS-silicone		(a)	60.0	85.0	91.0	62.5		
		After Test A →	(b$_1$)	51.0	79.0	90.0	62.5		
		After Tests A + C →	(b$_2$)	42.5	67.5	87.5	61.5		
1-3/4" square:									
2-13-0a	30g ZnO, SP 500 15cc PS7 30cc H$_2$O		(a)	31.5	96.0	98.5	98.0	0.132	0.98
			(b)	31.5	93.5	97.5	97.5	0.138	0.99
2-13-0	30g ZnO, SP 500 15cc PS7 30cc H$_2$O	Sprayed on organic Leonite-TiO$_2$ primer coat.	(a)	31.5	95.5	98.5	98.5	0.133	0.98
			(b)	32.5	93.5	98.0	98.0	0.139	0.99
2-9-0	15g ZnO, SP 500 7.5cc PS7 15cc H$_2$O	Two applications. First coat cured under standard conditions.	(a)	32.5	92.5	98.5	98.5	0.131	0.93
			(b)	30.5	89.5	97.5	98.0	0.136	0.95
2-12-3a	2g ZnO, SP 500 1cc PS7 1cc H$_2$O	Brush painted	(a)	29.5	94.5	98.0	97.5	0.146	
			(b)	29.0	90.5	96.0	96.5	0.150	
2-10-7a	20g ZnO, SP 500 20cc PS7 10cc H$_2$O	Pigment:binder = 2.15:1	(a)	22.5	88.5	89.5	88.5	0.258	0.93
			(b)	22.5	86.5	88.5	87.5	0.269	0.95

1. Reflectivity based on α -Al$_2$O$_3$ scale. Wavelengths chosen arbitrarily in visible range.
2. Reflectivity prior to space environment exposure.
3. Reflectivity after space environment exposure. 6. Aluminum Phosphate.
4. Water spotted during a maintenance stoppage in the run from spillage of condensed water on outside of chamber lid.
5. Sodium silicate, 1:3.22 (Philadelphia Quartz).
Note: Unless otherwise indicated, pigment/binder ratio was 4.3:1.
All samples air dried 18 hours, cured at 135°-145°C for 24 hours.

Table 15

LOSSES IN REFLECTIVITY FOR PIGMENTS AND ORGANIC VEHICLES DUE TO SOLAR SIMULATION

No. of Coating	Paint Vehicle	Pigment	Time of Exposure	Reflectivity,[1] % at			
				380 mμ	440 mμ	600 mμ	700 mμ
27	Teflon TFE 30 (X)	CaSiO$_3$	(a)[2]	82.6	84.7	78.6	74.8
			(b)[3]	36.0	48.9	69.4	70.7
30	Teflon TFE 30 (X)	ZrO$_2$	(a)	75.4	87.8	70.0	66.5
			(b)	30.0	42.0	59.6	61.7
34	Teflon TFE 30 (X)	Al$_2$O$_3$	(a)	77.1	76.6	66.4	61.9
			(b)	38.0	47.9	58.9	58.1
56	Teflon TFE 30 (X) (on glass)	–	(a)	86.8	84.2	64.8	52.6
			(b)[4]	58.7	63.5	57.7	48.1
			(c)	42.6	48.7	54.1	47.8
67	Teflon TFE 30 (X)	–	(a)	77.8	73.5	64.4	63.6
			(b)	62.0	63.0	59.5	60.9
			(c)	51.3	53.0	55.7	59.7
68	Teflon TFE 30 (X)	–	(a)	85.0	84.7	80.6	78.0
			(b)	65.4	69.2	74.7	74.8
113	Kel-F 800 (XVI)	ZnO	(a)	28.5	82.8	75.0	70.9
			(b)	21.5	57.7	68.5	67.7
116	Kel-F 800 (XVI)	ZnO	(a)	30.0	84.4	77.7	73.8
			(b)	23.5	63.2	72.7	71.3
117	Kel-F 800 (XVI)	ZnO	(a)	30.5	84.6	78.5	74.4
			(b)	22.6	62.1	72.3	71.6
118	Kel-F 800 (XVI)	ZnO	(a)	30.0	84.0	77.6	73.5
			(b)	23.5	64.8	72.7	71.0
121	Teflon FEP 120 (XIV)	ZnO	(a)	40.0	84.2	77.3	73.5
			(b)	37.4	73.0	75.0	73.0
			(c)	25.1	52.4	67.5	69.6

Table 15 (Cont.)

No. of Coating	Paint Vehicle	Pigment	Time of Exposure	Reflectivity,[1] % at			
				380 mμ	440 mμ	600 mμ	700 mμ
124	Kynar Vinylidene Fluoride (XXII)	ZnO	(a)	35.3	79.8	74.0	70.4
			(b)	31.3	70.3	71.6	69.4
			(c)	23.4	47.0	62.5	65.1
125	Kynar Vinylidene Fluoride (XXII)	ZnO	(a)	33.8	83.4	78.3	75.3
			(b)	31.0	69.6	74.5	73.6
			(c)	20.0	40.0	60.6	66.2
126	Kynar Vinylidene Fluoride (XXII)	ZnO	(a)	33.5	84.5	80.2	77.6
			(b)	30.4	71.8	77.4	76.5
			(c)	20.2	38.4	60.8	67.0
403-1	Leonite 201-S (XLIII)	TiO$_2$	(a)	14.0	90.9	92.8	91.1
			(b)	14.0	85.2	89.2	87.6
405-2A	Leonite (XLIII) (0.5 hr cure)	ZnO	(a)	33.0	93.8	96.5	95.6
			(b)	26.2	76.5	93.7	94.5
			(c)	16.5	51.1	87.8	92.0
405-2B	Leonite (XLIII) (24 hr cure)	ZnO	(a)	32.0	92.2	96.7	96.6
			(b)	26.2	75.5	93.5	94.5
			(c)	18.2	53.0	88.5	92.8
406-1A	Leonite (XLIII) (0.5hr cure)	ZnS	(a)	60.5	86.4	89.6	64.5
			(b)	52.5	78.5	88.3	64.0
			(c)	39.2	62.5	85.0	64.0
406-1B	Leonite (XLIII) (24 hr cure)	ZnS	(a)	60.5	85.6	89.3	64.5
			(b)	52.0	77.3	87.7	64.0
			(c)	39.2	62.5	84.7	64.0
153	Kel F 800 (XVI) and Teflon 7 (IX)	ZnO	(a)[5]	28.0	86.0	84.0	81.0
			(d)[5]	15.0	41.5	64.0	69.0
154	Exon 461 (XXIII)	ZnO	(a)	30.0	85.0	80.5	78.0
			(d)	6.0	10.0	31.5	43.0

Table 15 (Cont.)

No. of Coating	Paint Vehicle	Pigment	Time of Exposure	Reflectivity,[1] % at			
				380 mμ	440 mμ	600 mμ	700 mμ
157	Kynar Vinylidene Fluoride (XXII)	ZnO	(a)	36.0	84.0	90.0	93.5
			(d)	30.0	64.0	81.0	87.5
158	Viton B (Cloudy) (XXV)	ZnS	(a)	49.5	77.0	91.5	75.0
			(d)	31.0	43.5	69.5	67.0
160	Kel F 800 (XVI)	ZnS	(a)	67.0	89.5	92.0	72.0
			(d)	39.5	49.5	78.0	64.0
164	Exon 461 (XXIII)	ZnS	(a)	63.0	86.0	89.0	68.0
			(d)	25.5	38.0	64.5	60.0
169	Teflon TFE 852-202 (XIII)	ZnO	(a)	67.5	84.0	91.5	74.5
			(d)	31.5	46.0	74.5	69.0
176	Viton A (XXIV)	ZnO	(a)	31.0	88.0	94.0	93.0
			(d)	26.0	68.0	87.5	90.0
178	Kel F 800 (XVI)	ZnS	(a)	65.0	87.5	90.5	71.5
			(d)	38.0	47.0	67.5	64.5
179	Kel F 800 (XVI)	ZnS	(a)	63.5	86.5	92.5	72.0
			(d)	38.0	48.0	79.0	65.5
180	Viton B (Semi-clear) (XXVI)	ZnO	(a)	25.5	85.0	94.5	95.0
			(d)	25.0	65.0	86.0	89.5
181	Viton B (Clear) (XXVII)	ZnO	(a)	27.5	88.0	89.5	88.0
			(d)	25.0	74.5	86.5	87.0
183	Kel F 8213 (XVII)	ZnO	(a)	26.5	88.0	86.5	84.5
			(d)	17.0	52.5	72.5	78.0

Table 15 (Cont.)

No. of Coating	Paint Vehicle	Pigment	Time of Exposure	Reflectivity,[1] % at			
				380 mμ	440 mμ	600 mμ	700 mμ
185	Kel F 8213 (XVII) (aqueous dispersion)	ZnO	(a)	25.5	87.0	87.5	85.5
			(d)	17.0	52.0	72.5	77.0
187	RTV-11 Silicone (IV)	None	(a)	64.5	73.5	77.5	75.5
			(d)	39.5	60.5	76.0	75.5
189	Viton B (Clear) (XXVII)	ZnO	(a)	30.0	88.5	90.0	88.0
			(d)	26.0	76.0	87.0	87.5
191	Viton B (Clear) (XXVII)	ZnO	(a)	30.0	89.0	93.5	91.5
			(d)	27.5	79.5	90.0	90.0
192	RTV-11 Silicone (IV)	ZnO	(a)	26.0	91.0	92.0	90.5
			(d)	26.0	86.0	91.5	90.0
194	Kel F 8213 (XVIII) (modified dispersion in ketone)	ZnO	(a)	37.0	95.5	97.5	96.5
			(d)	32.0	82.5	93.5	95.0
196	Kel F 8213 (XVIII)	ZnO	(a)	35.0	93.5	96.0	94.5
			(d)	30.0	79.5	91.5	93.0
197	LTV-602 Silicone (V)	ZnO	(a)	31.5	94.0	95.5	94.5
			(d)	31.0	93.0	94.5	93.0
407-2	Leonite 201-S (XLIII)	MgO	(a)	89.5	93.5	92.5	91.0
			(d)	18.5	35.0	78.5	85.5
409-2B	Leonite (XLIII)	BN	(a)	81.0	85.0	88.5	87.5
			(d)	25.0	38.0	75.0	82.0
410-1	Leonite (XLIII)	Sb_2O_3	(a)	74.5	85.0	88.0	85.5
			(d)	23.5	33.0	60.5	69.5

Table 15 (Con. t)

No. of Coating	Paint Vehicle	Pigment	Time of Exposure	Reflectivity,[1] % at			
				380 mμ	440 mμ	600 mμ	700 mμ
410-2	Leonite (XLIII)	$Bi_2O_2CO_3$	(a)	82.5	90.0	94.0	93.0
			(d)	25.0	30.0	44.0	53.0
413-2	Silicone 806A (VIII)	MgO	(a)	83.5	90.0	91.5	90.5
			(d)	9.0	25.0	80.0	86.5
413-3	Silicone (VIII)	ZnO	(a)	26.0	89.0	87.5	85.0
			(d)	17.0	56.0	83.5	83.5
414-2	Silicone (VIII)	MgO	(a)	88.5	93.5	94.5	94.0
			(d)	8.5	24.0	80.5	88.5
416-1	Leonite (XLIII)	ZnO	(a)	26.0	86.0	85.0	83.0
			(d)	21.0	71.0	83.0	81.5
416-2	Silicone (VIII)	ZnO	(a)	24.0	86.5	84.0	81.5
			(d)	12.5	46.0	79.0	80.5

[1] Reflectivity based on MgO scale. Wavelengths chosen arbitrarily in visible range.

[2] Reflectivity prior to space environment exposure (a).

[3] Reflectivity after exposure to 4 times solar radiation intensity in a vacuum for 18.5 hr (Test D)

[4] Reflectivity after exposure to 4 suns in a vacuum for 78.5 hr (Test E)

[5] Reflectivity after exposure to 4 suns in a vacuum for 27 hr (Test F)
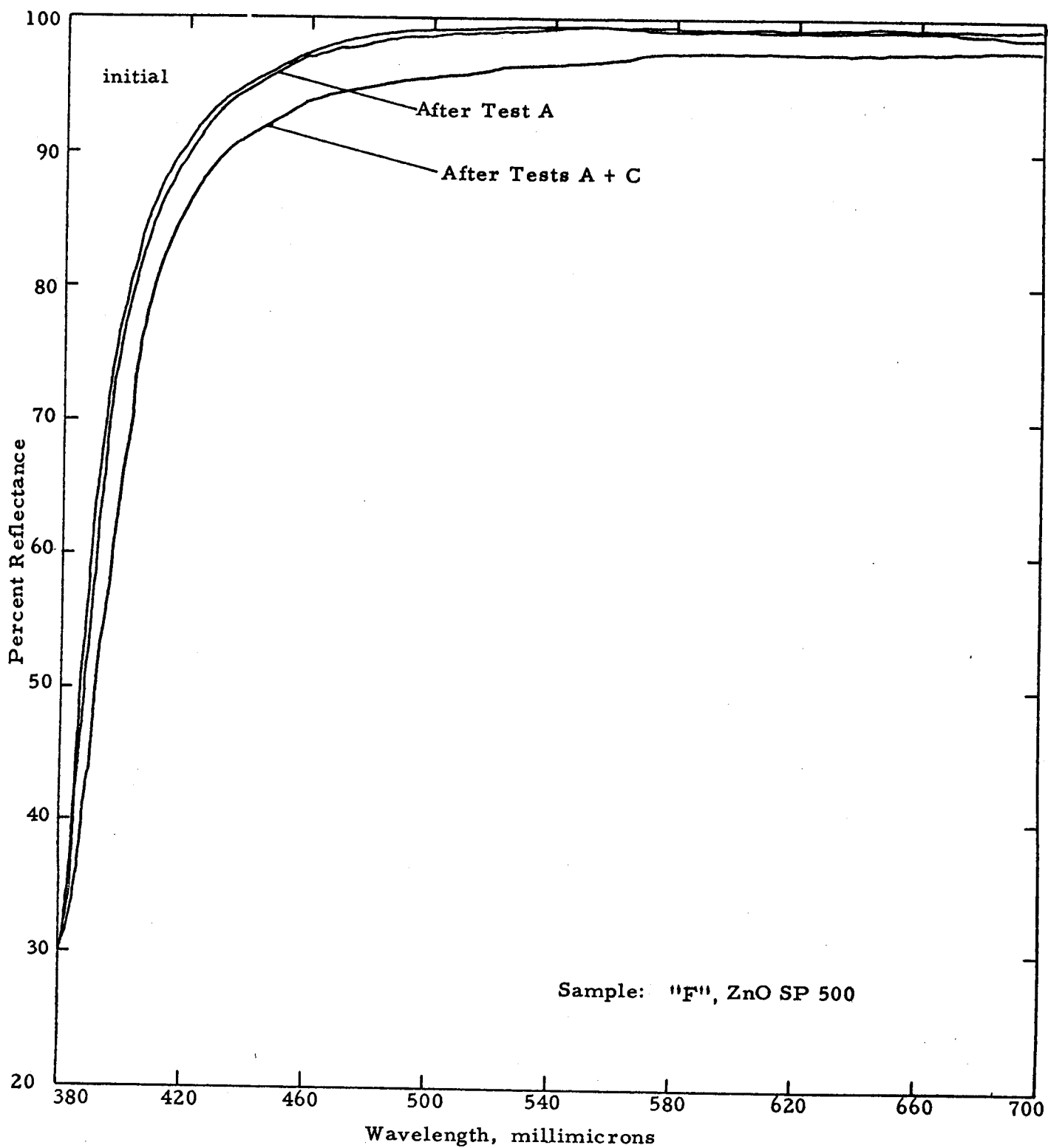
Figure 7 - Reflectance Changes on Space Simulation for ZnO Pigment
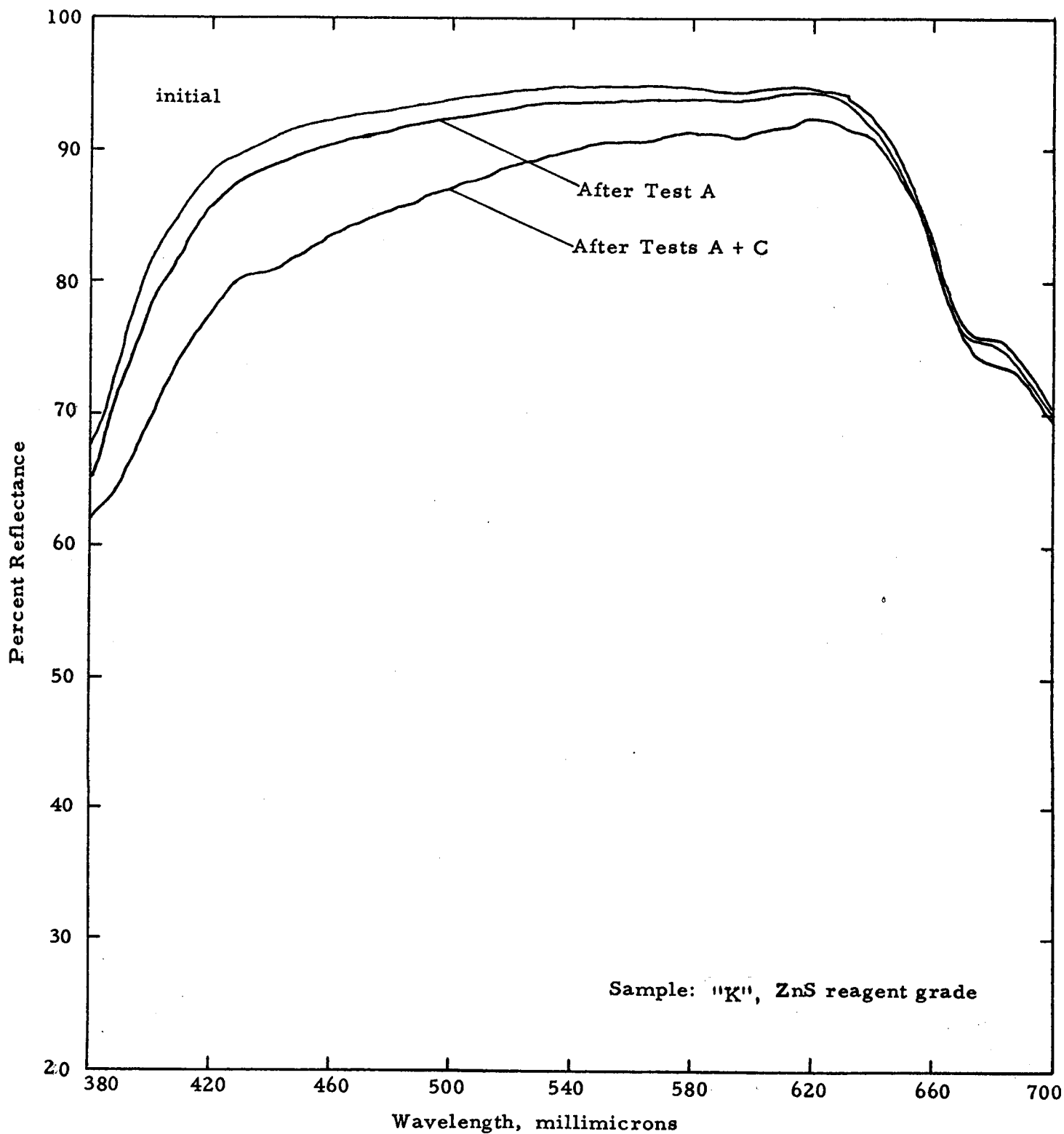
Figure 8 - Reflectance Changes on Space Simulation for ZnS Pigment
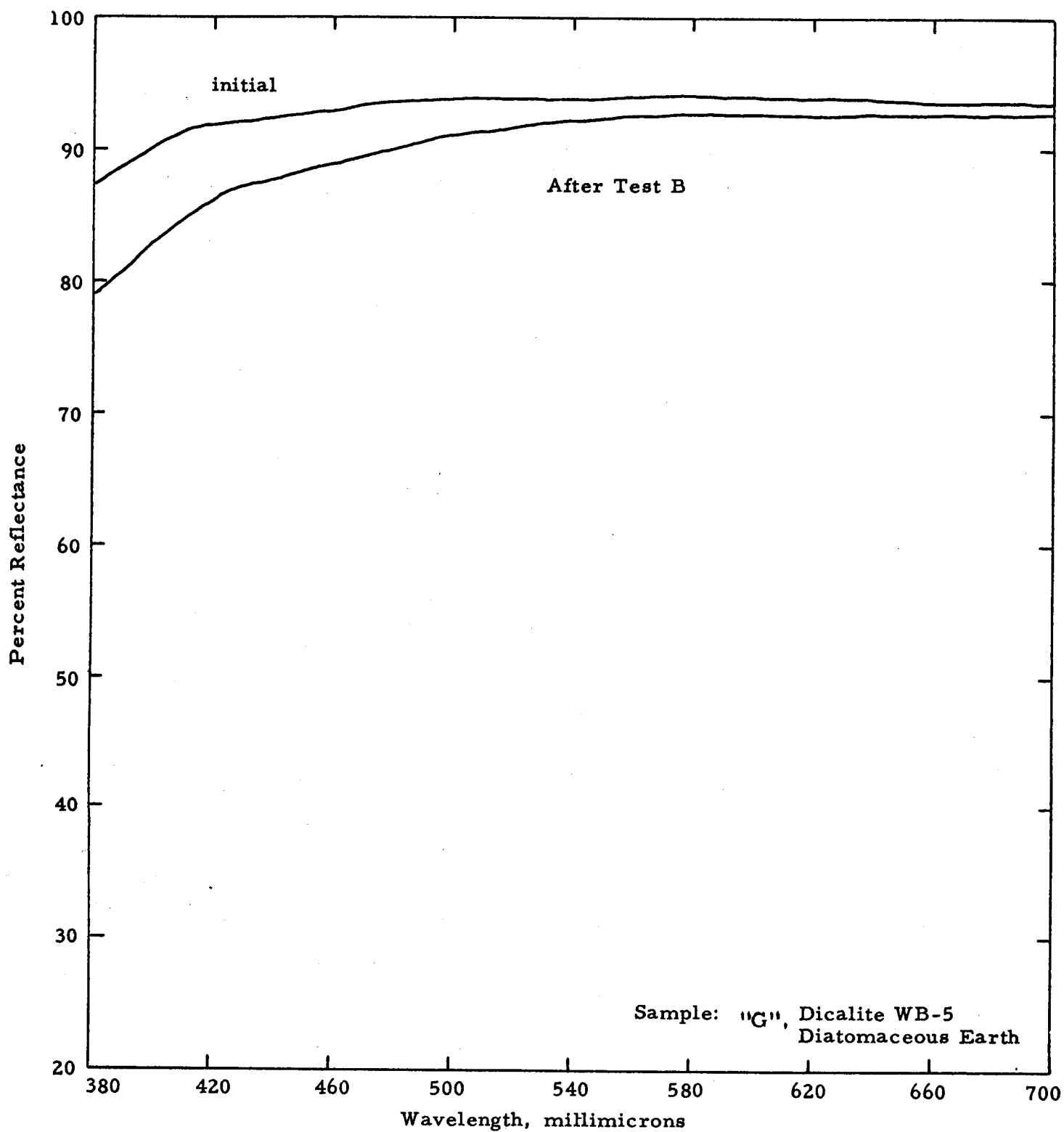
Figure 9 - Reflectance Changes on Space Simulation for Diatomaceous Earth
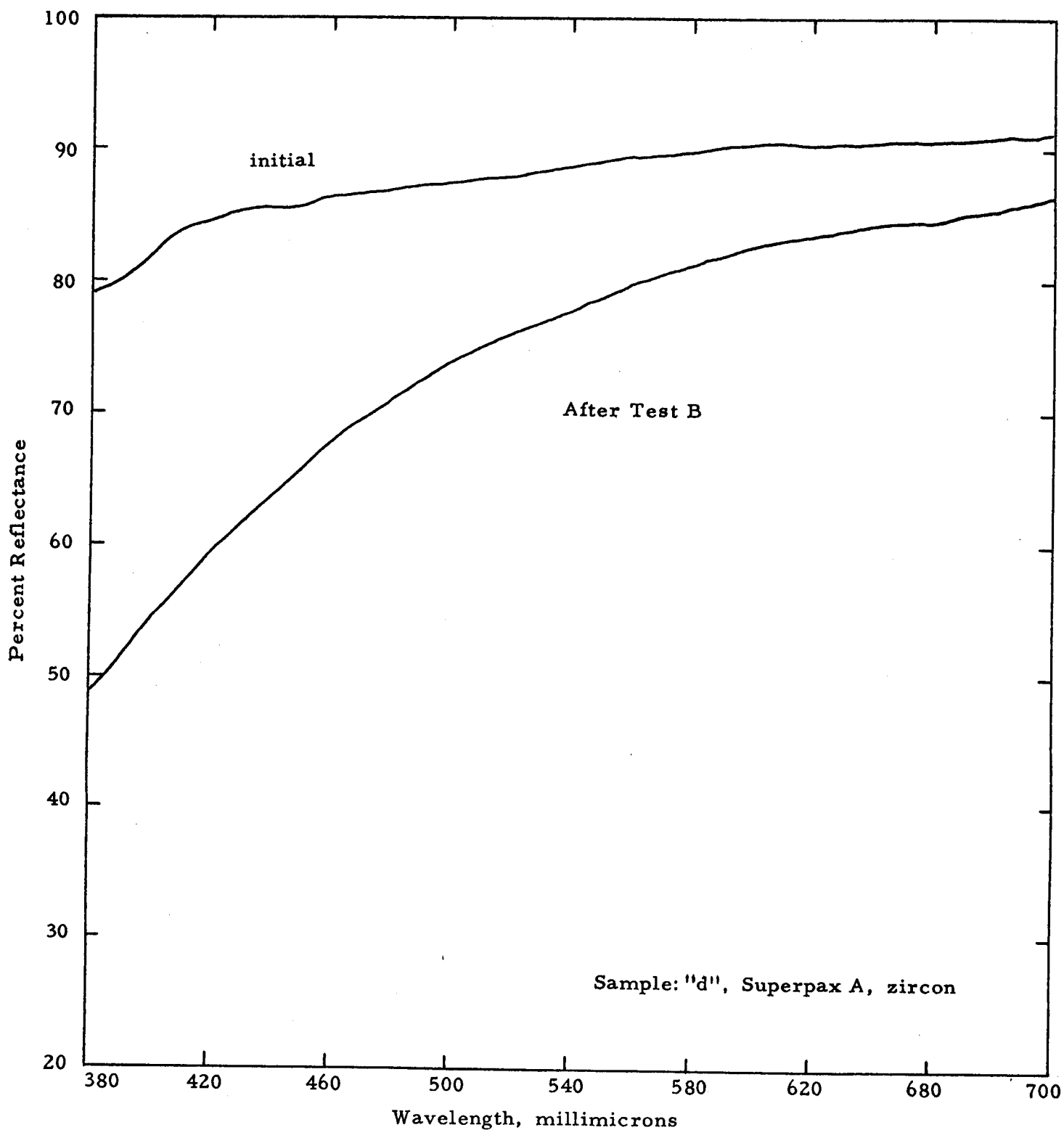
Figure 10 - Reflectance Changes on Space Simulation for $ZrSiO_4$ Pigment
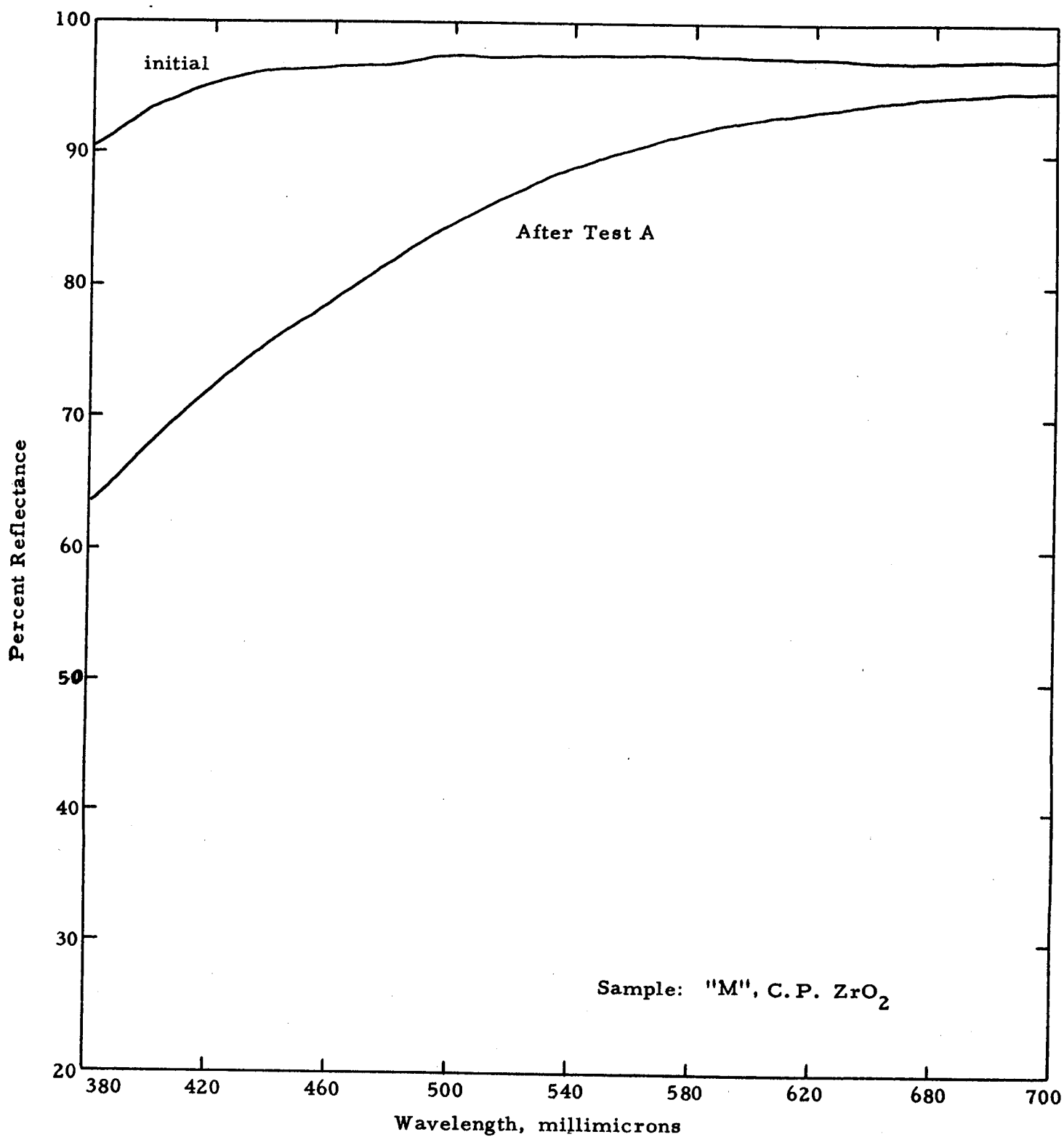
Figure 11- Reflectance Changes on Space Simulation for ZrO_2 Pigment
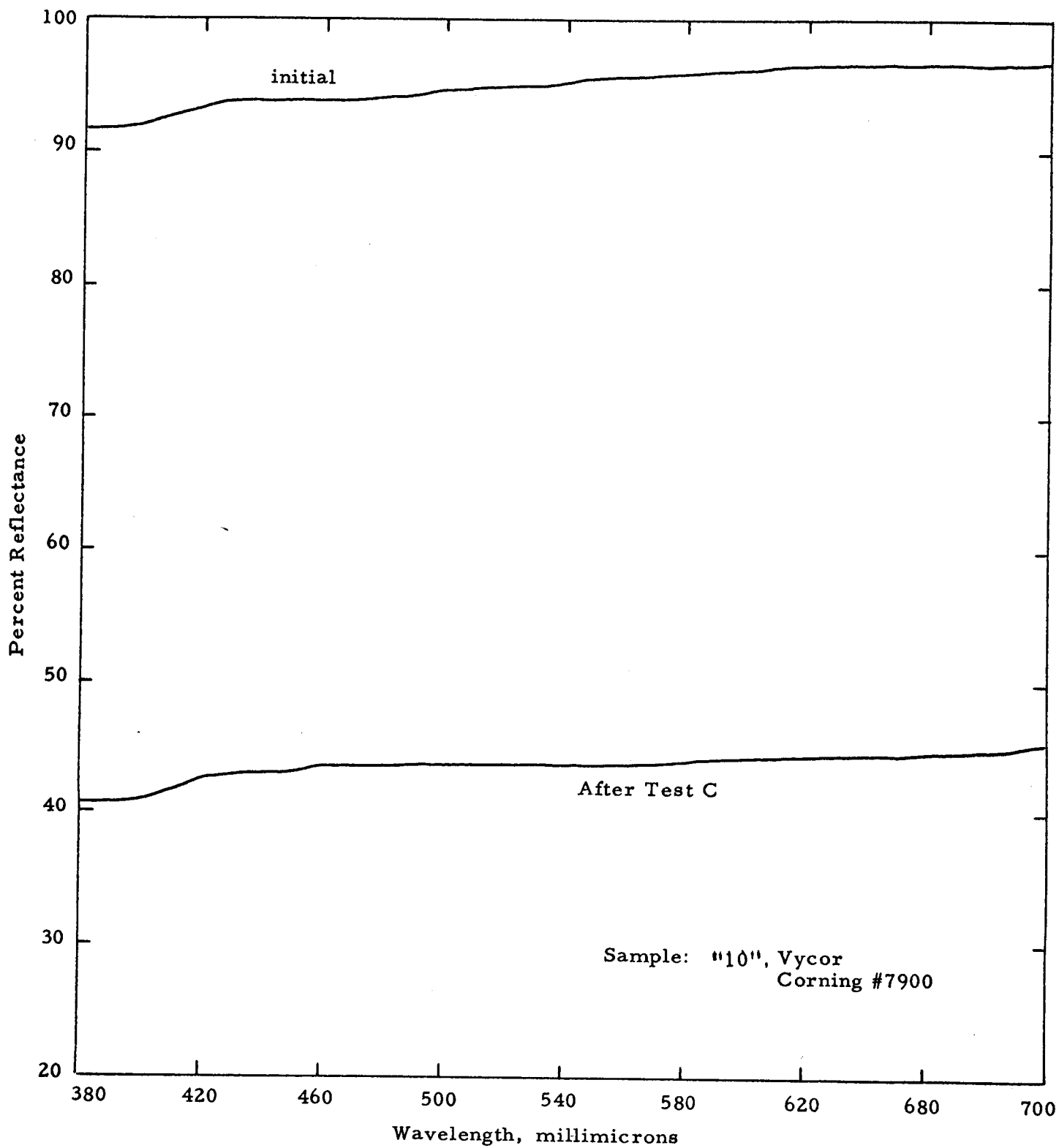
Figure 12 - Reflectance Changes on Space Simulation for Vycor Pigment
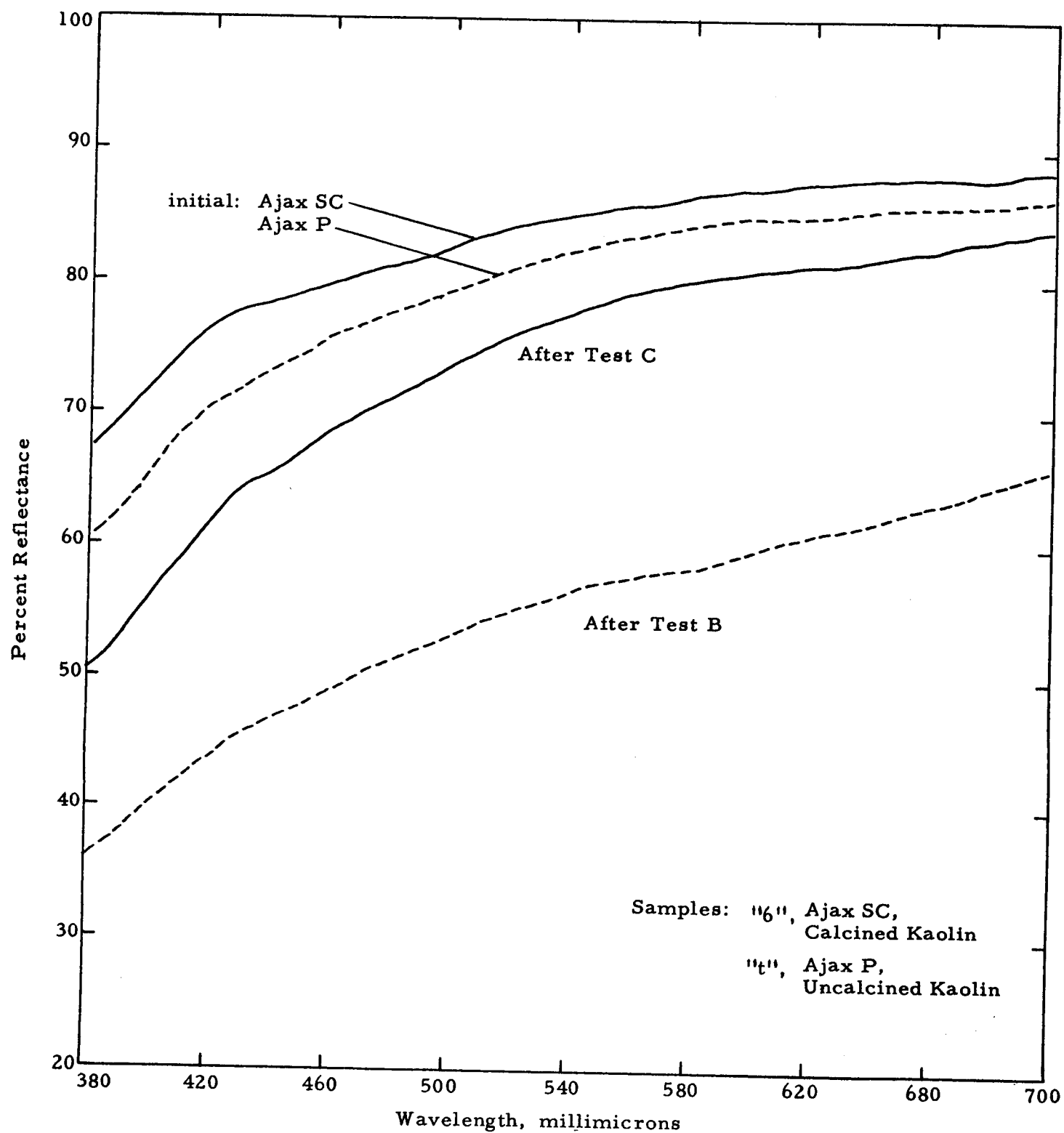
Figure 13- Reflectance Changes on Space Simulation for Kaolin Pigments
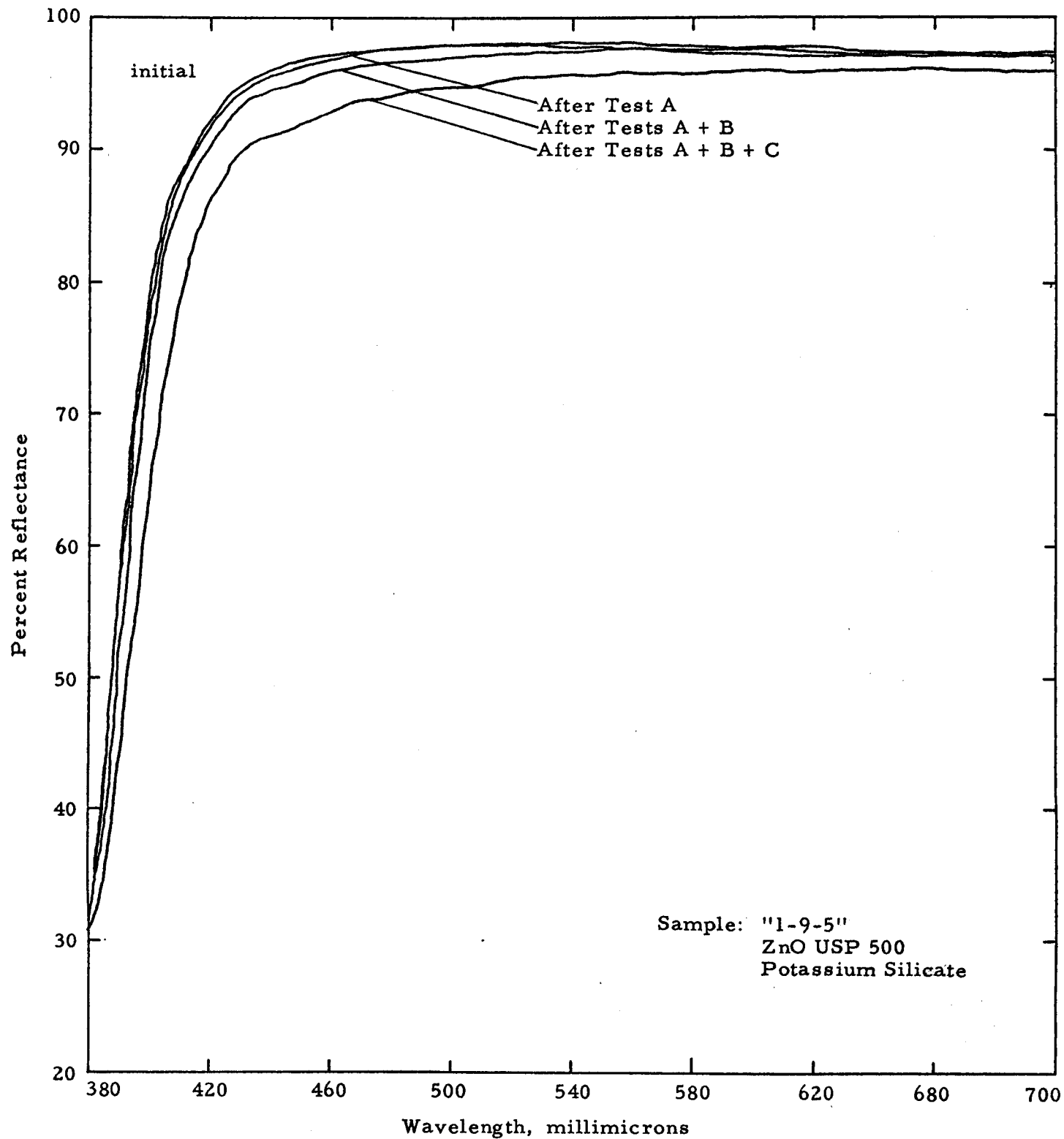
Figure 14a-Reflectance Changes on Space Simulation for
ZnO-Potassium Silicate Paint

Figure 14b - Reflectance Changes for Absorptivity Determinations:
ZnO-Potassium Silicate Paint

Absorptivity (α):
initial - 0.149
after Test α - 0.156
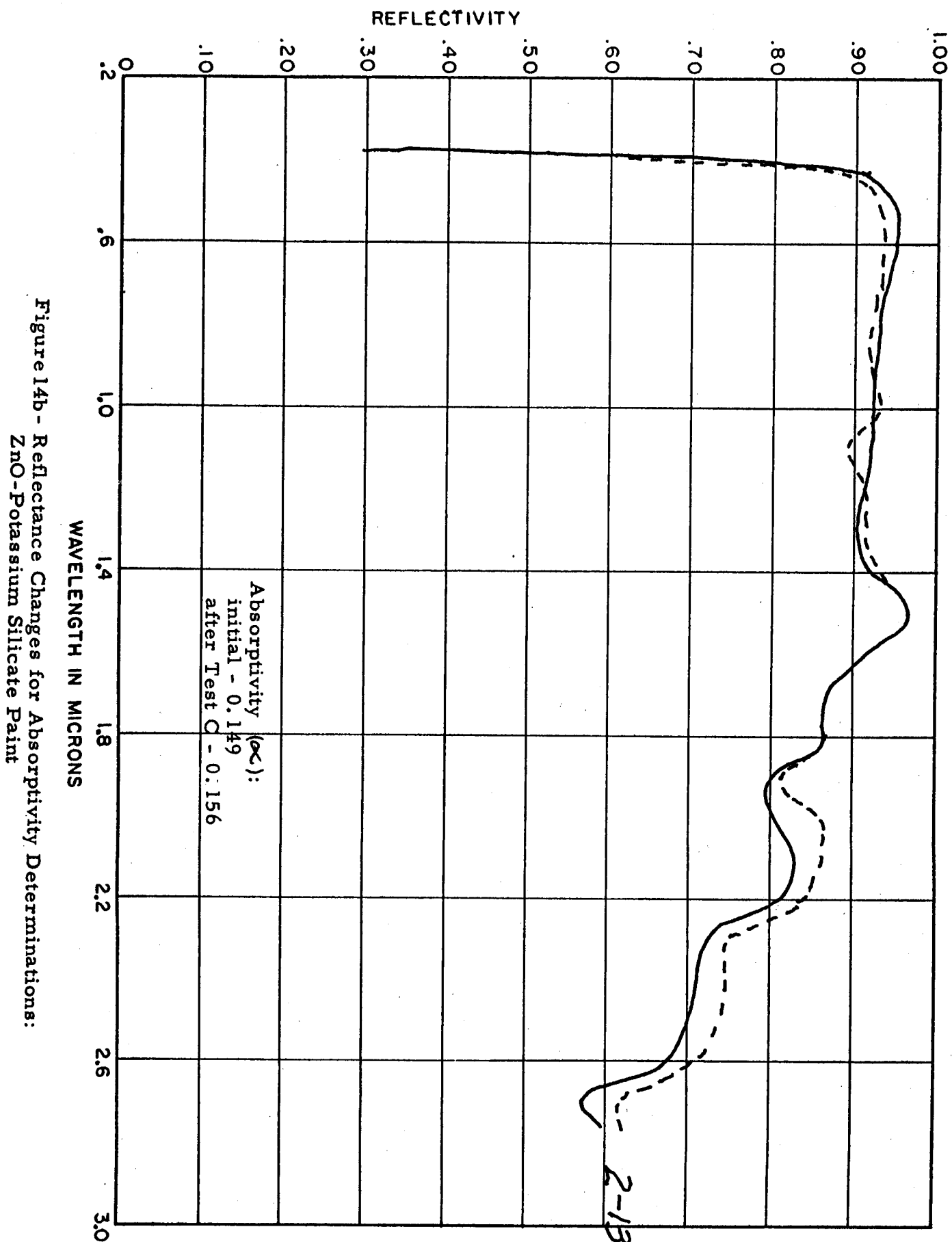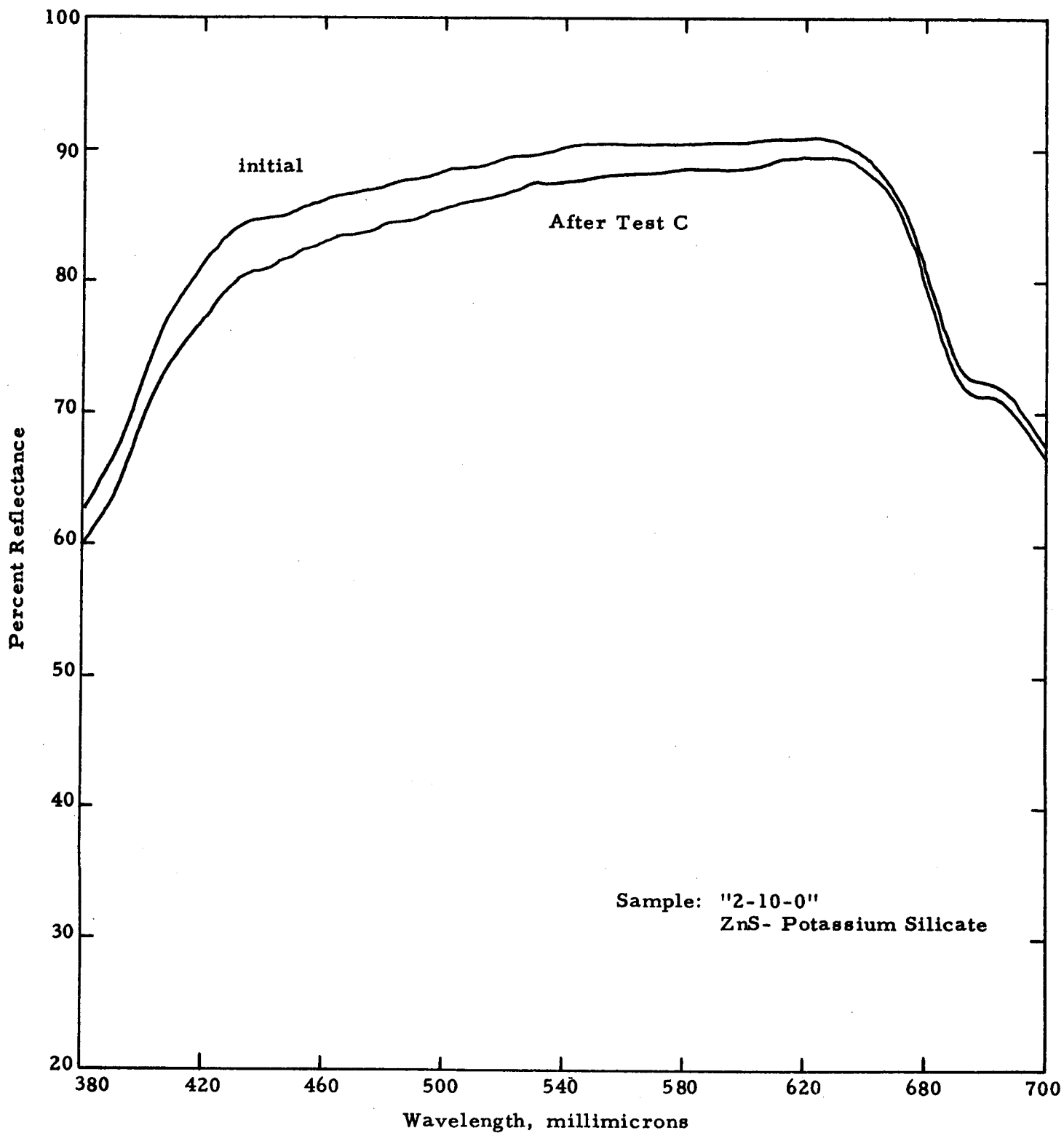
Figure 15a- Reflectance Changes on Space Simulation for
ZnS-Potassium Silicate Paint
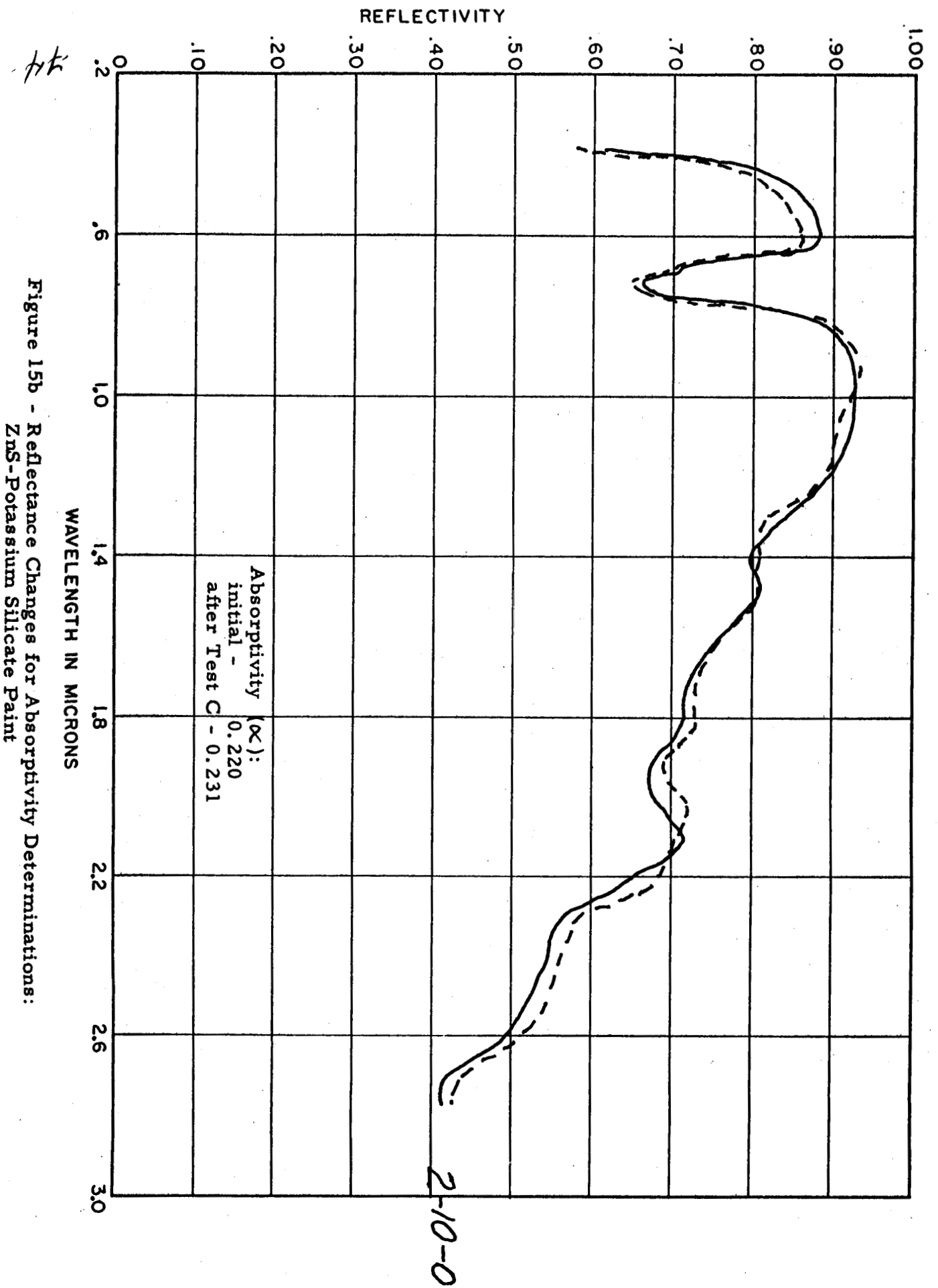
Figure 15b – Reflectance Changes for Absorptivity Determinations:
ZnS-Potassium Silicate Paint

Absorptivity (α):
initial – 0.220
after Test C – 0.231
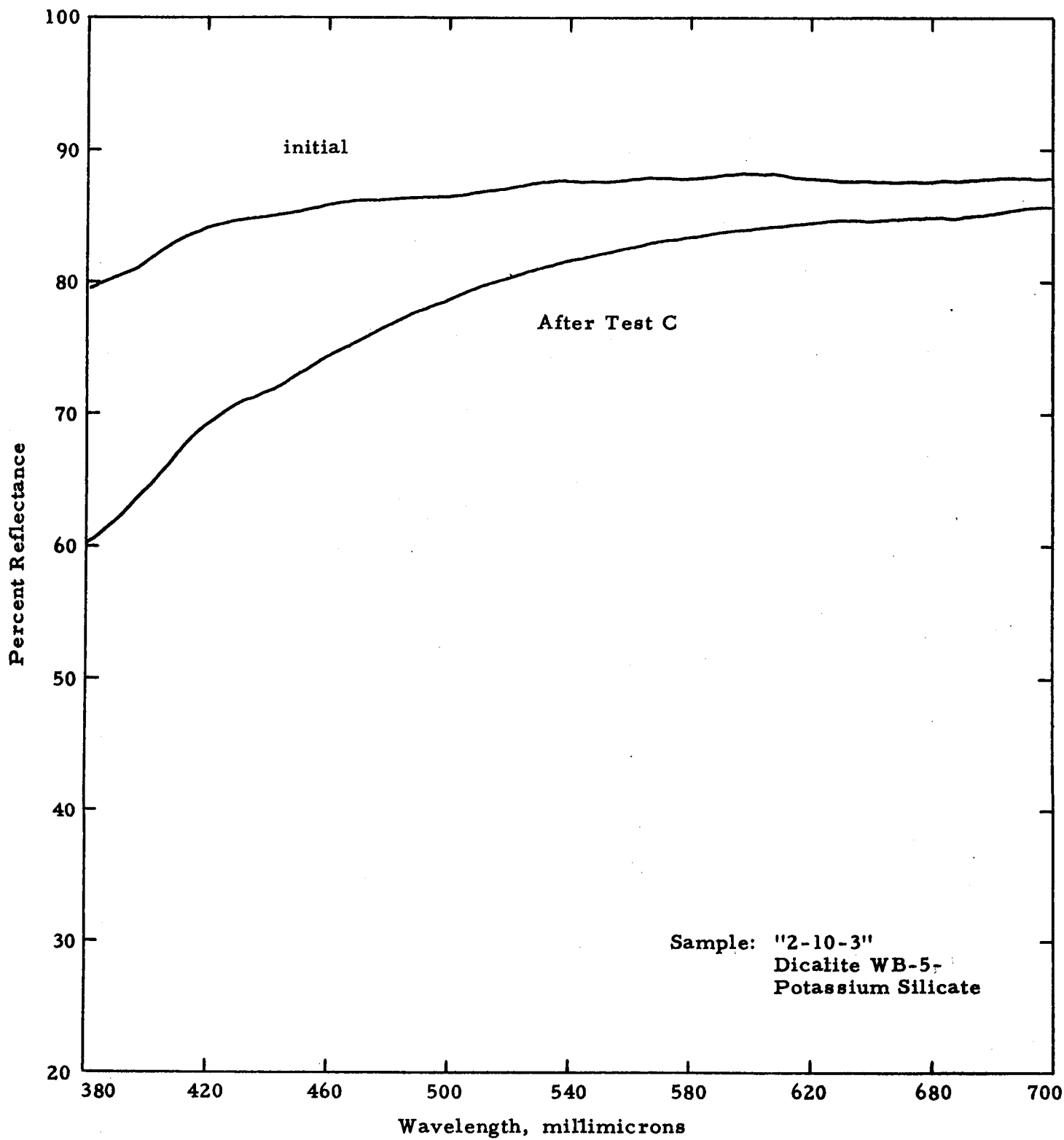
Figure 16a- Reflectance Changes on Space Simulation for
Diatomaceous Earth-Potassium Silicate Paint
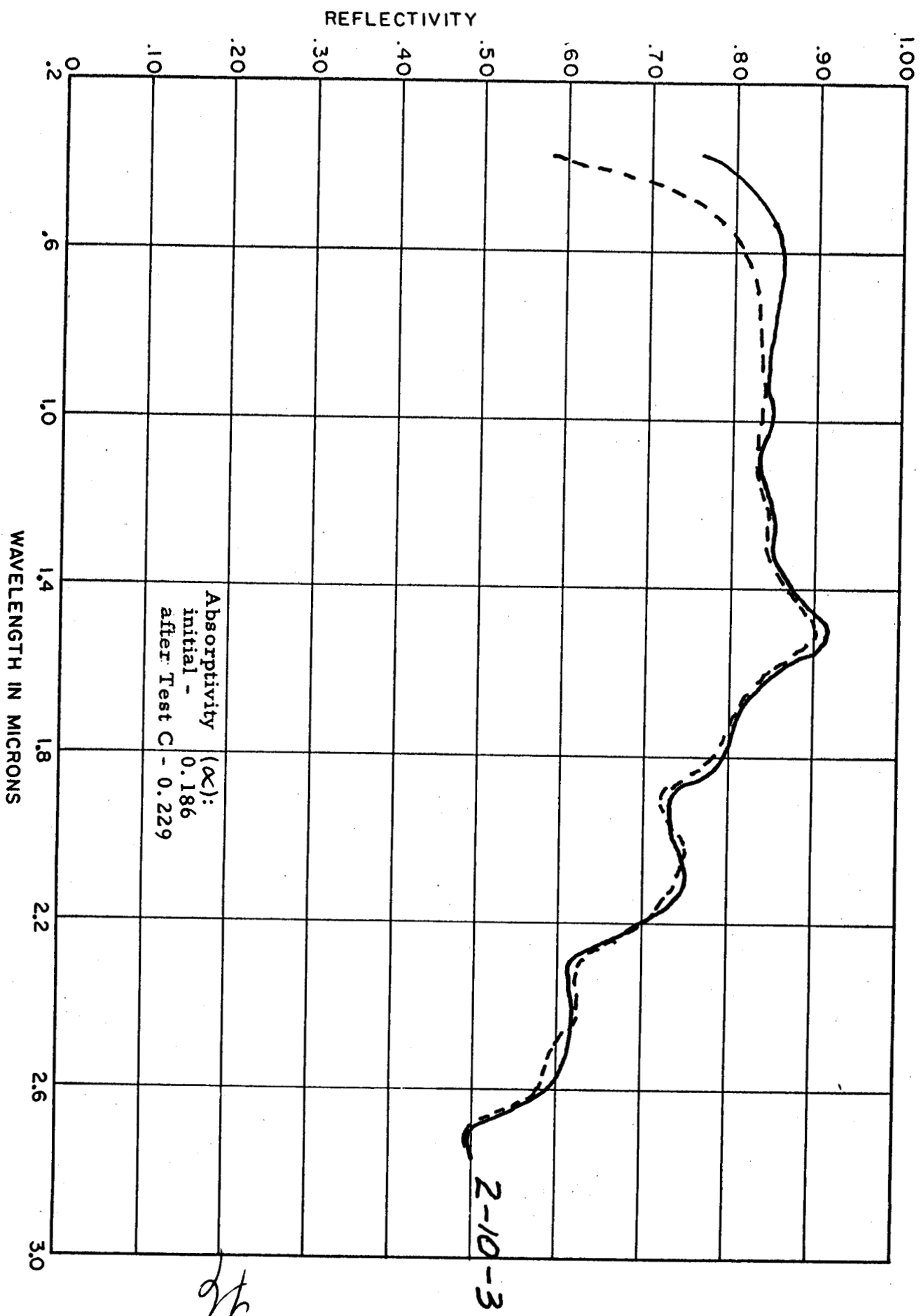
Figure 16b - Reflectance Changes for Absorptivity Determinations:
Diatomaceous Earth-Potassium Silicate Paint

Absorptivity (α):
initial - 0.186
after Test C - 0.229
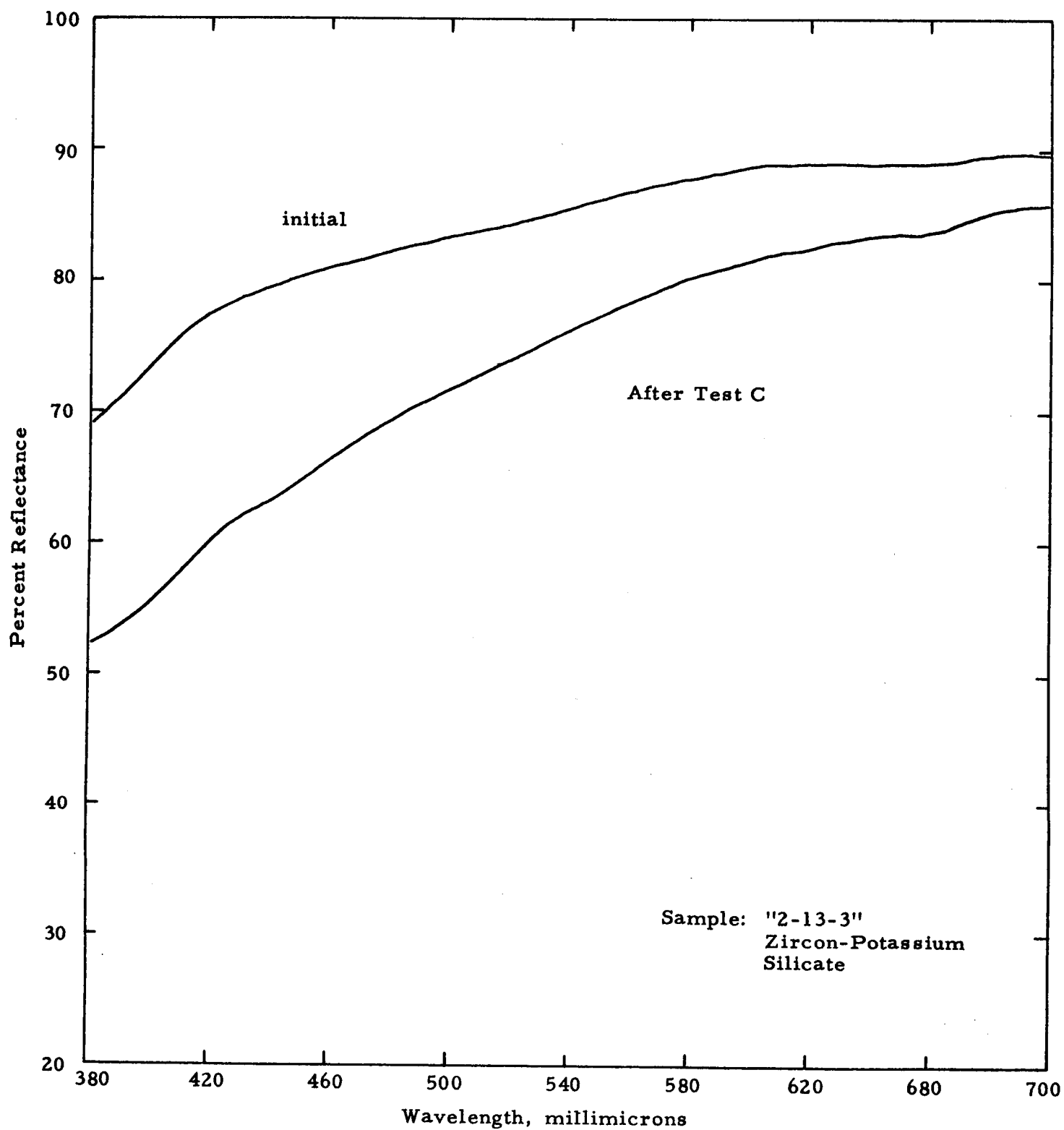
Figure 17a- Reflectance Changes on Space Simulation for
$ZrSiO_4$-Potassium Silicate Paint

Figure 17b - Reflectance Changes for Absorptivity Determinations:
ZrSiO$_4$-Potassium Silicate Paint

Absorptivity (α):
initial - 0.180
after Test C - 0.249
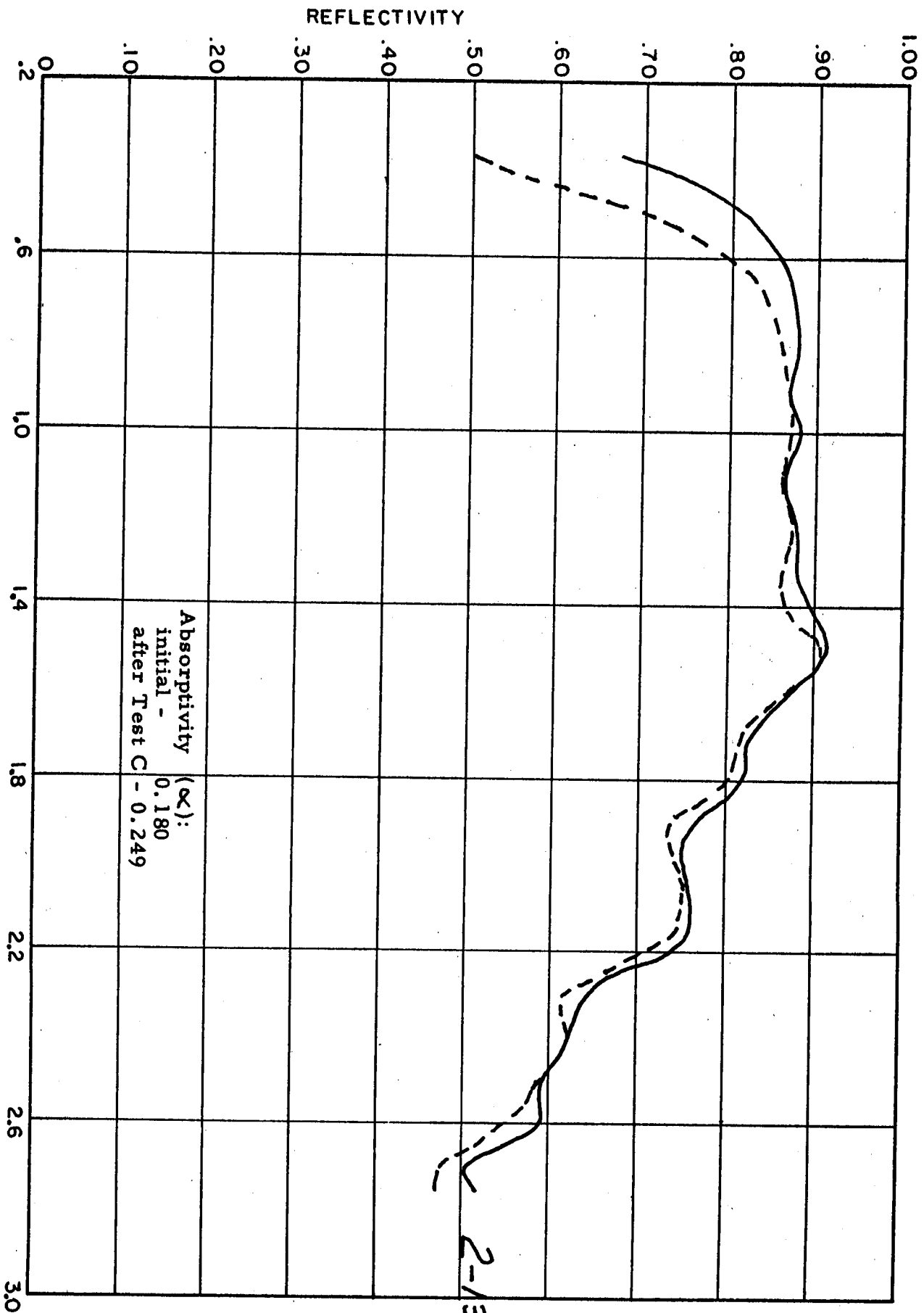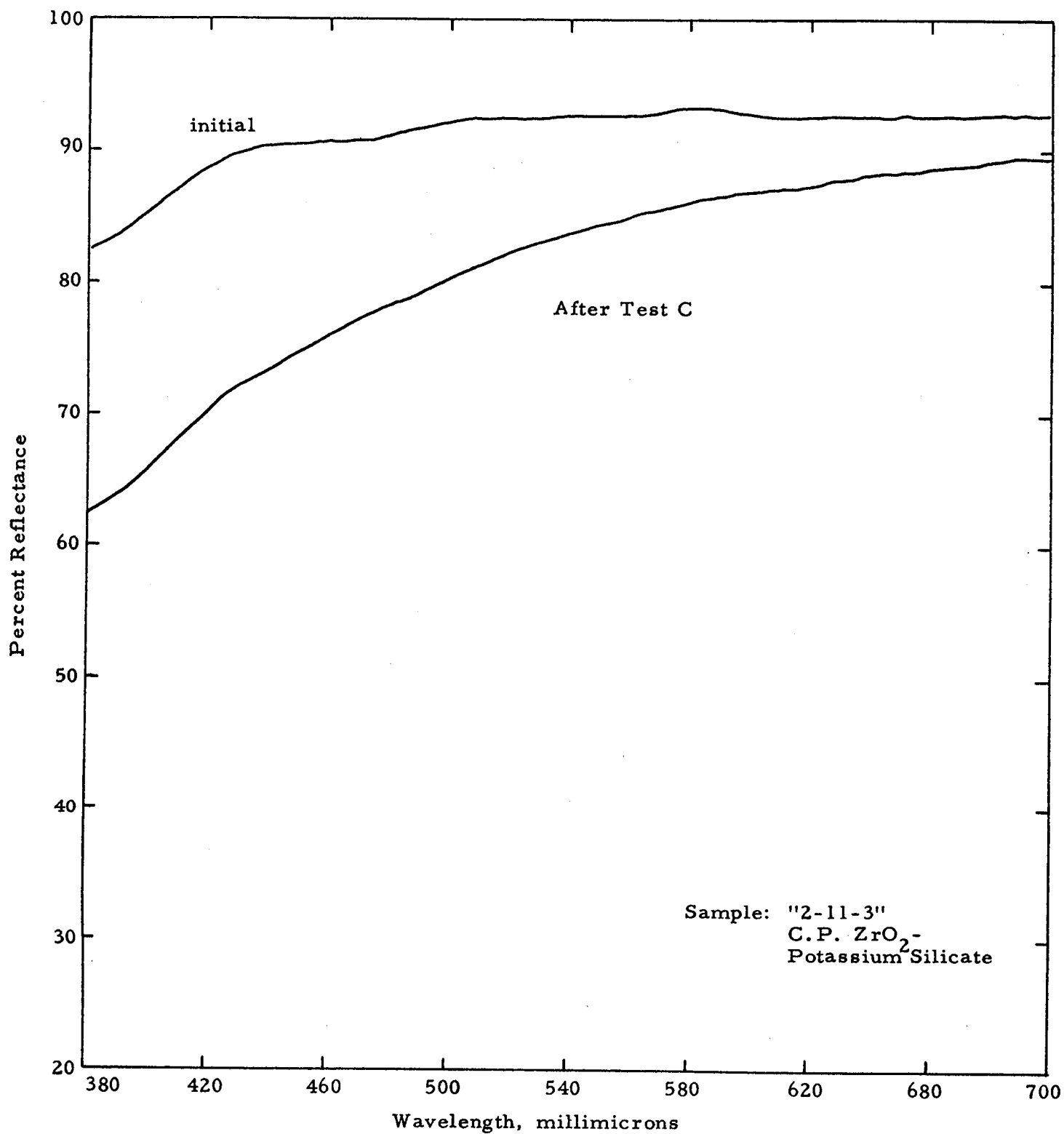
Figure 18a- Reflectance Changes on Space Simulation for
ZrO_2-Potassium Silicate Paint
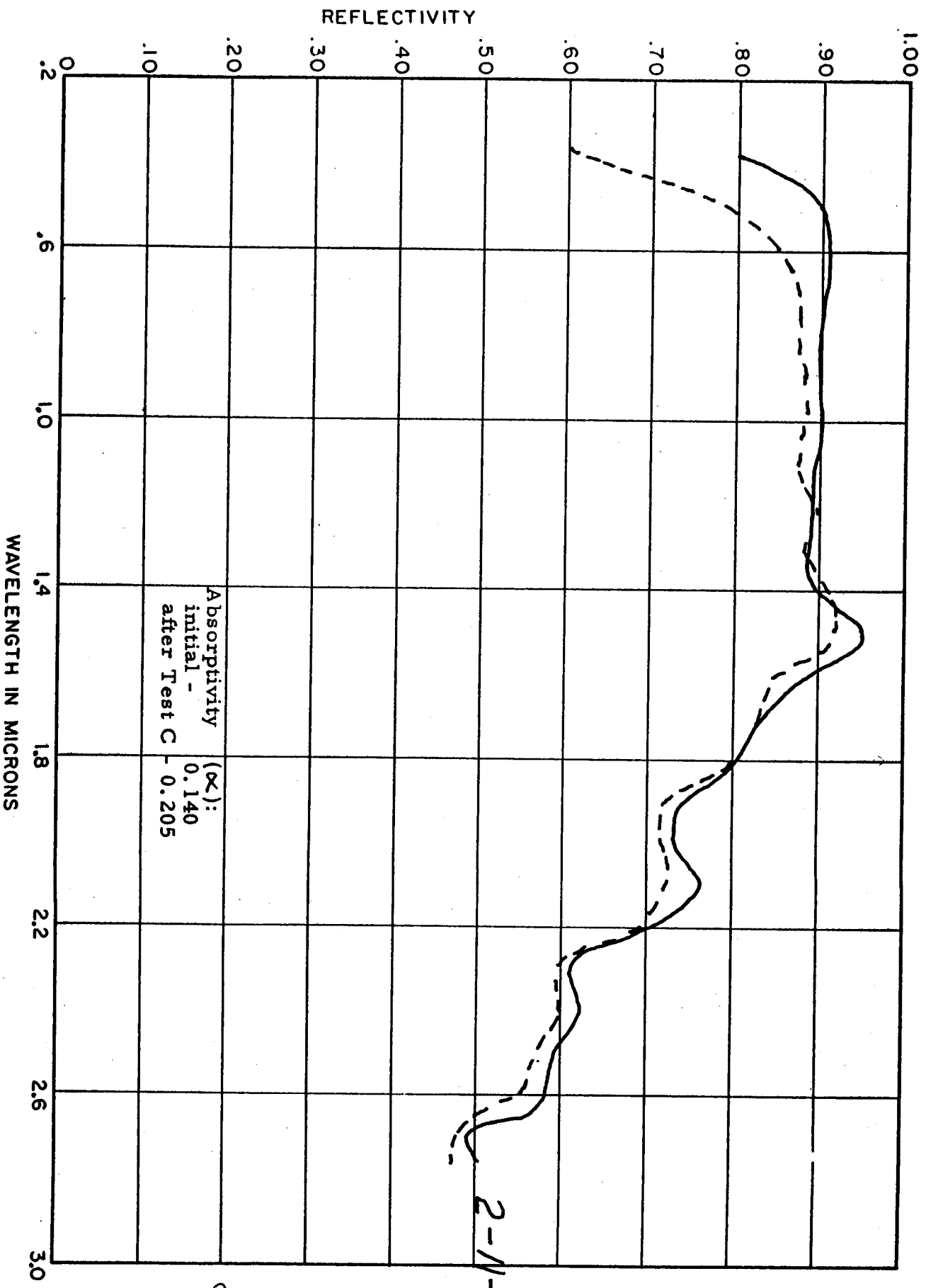
Figure 18b - Reflectance Changes for Absorptivity Determinations:
ZrO$_2$- Potassium Silicate Paint

Absorptivity (α):
initial - 0.140
after Test C - 0.205

2-N-3
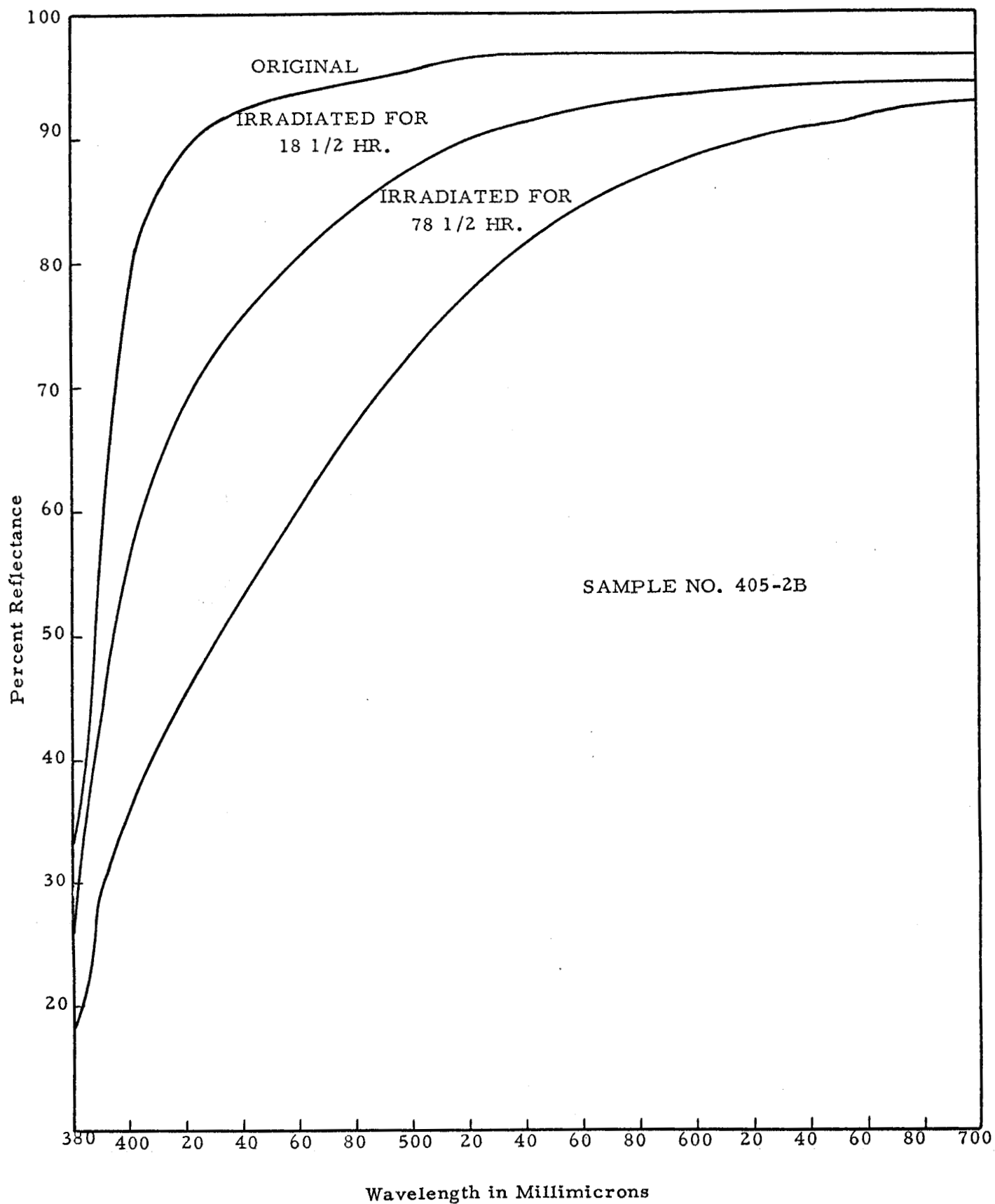
FIGURE 19 – REFLECTANCE CHANGES ON SPACE SIMULATION FOR
ZnO-LEONITE 201-S PAINT, CURED FOR 24 HRS. AT 257°F
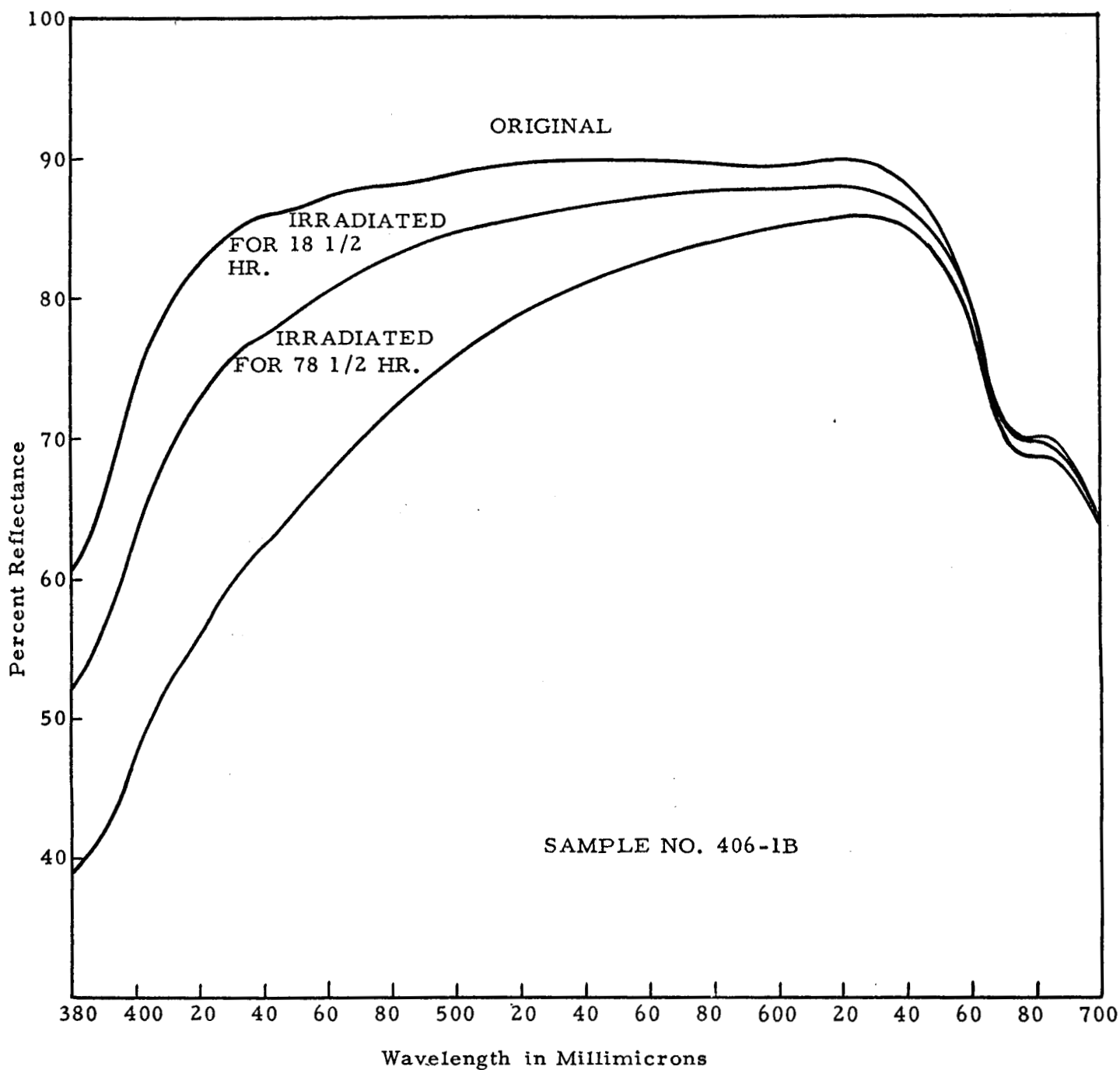
FIGURE 20 - REFLECTANCE CHANGES ON SPACE SIMULATION FOR ZnS-
LEONITE 201-S PAINT, CURED FOR 24 HRS. AT 257°F
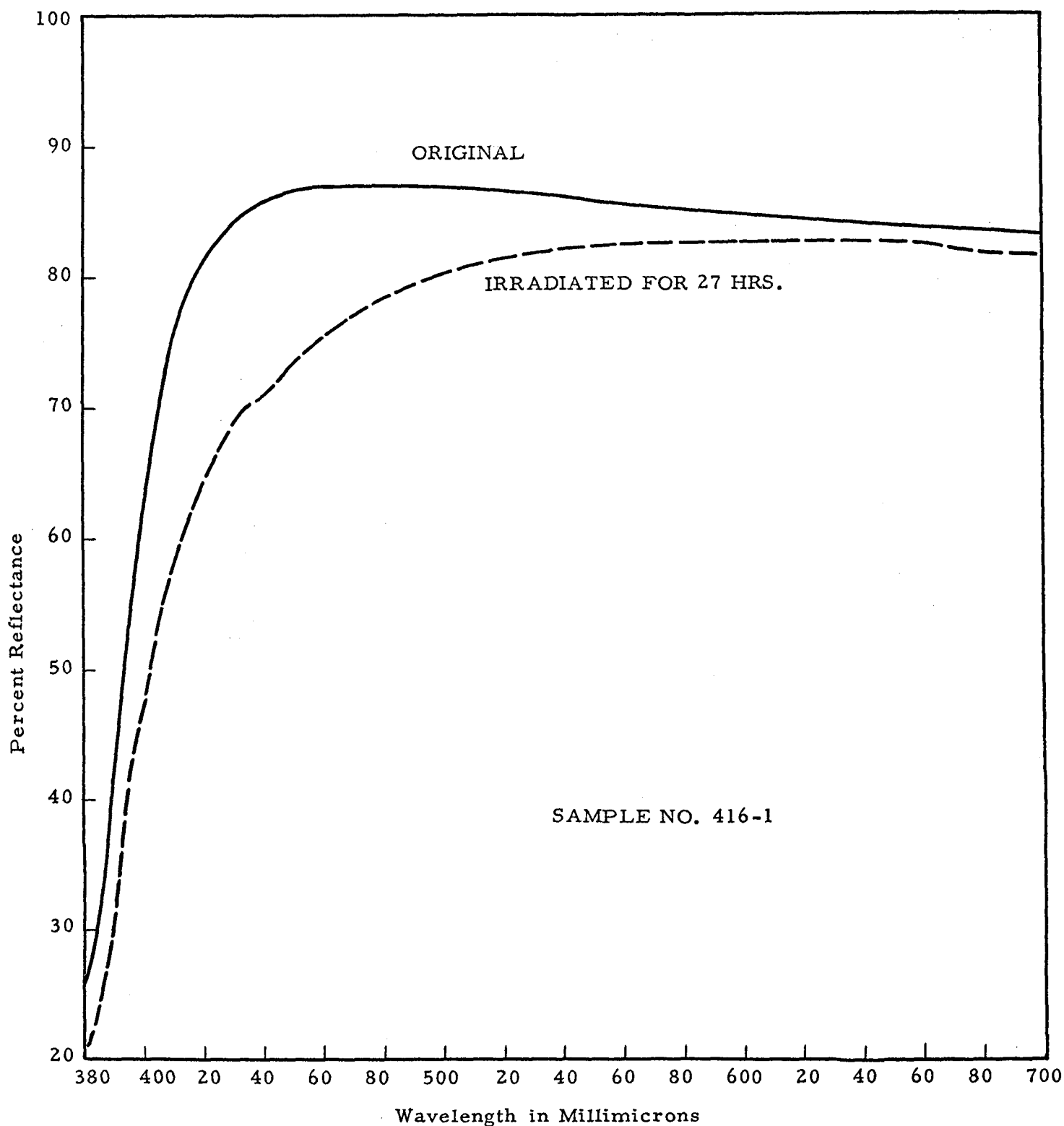
FIGURE 21 - REFLECTANCE CHANGES ON SPACE SIMULATION FOR ZnO-
LEONITE 201-S PAINT, CURED AT ROOM TEMPERATURE AND
FOR 0.5 HR. AT 257°F
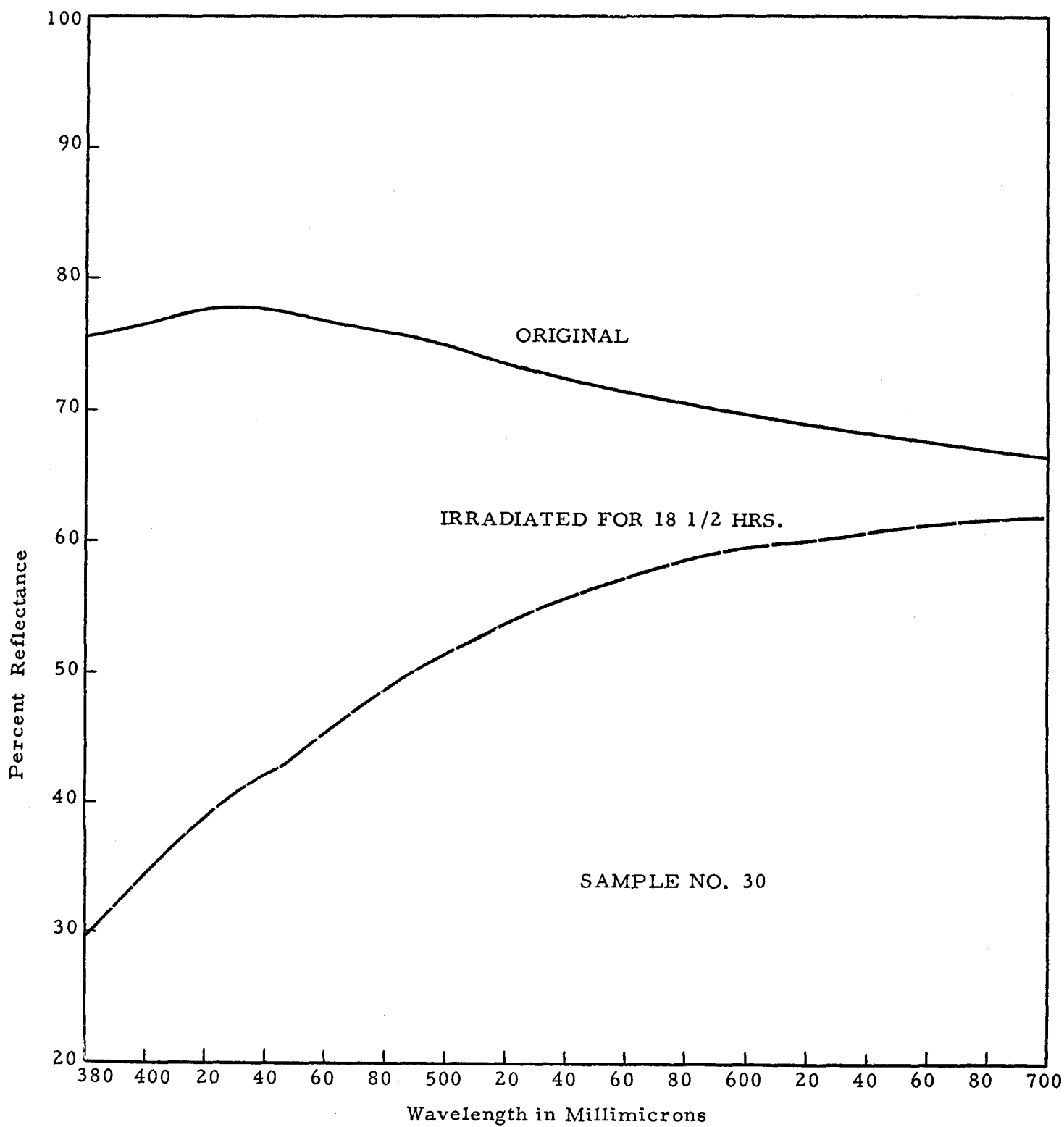
FIGURE 22 - REFLECTANCE CHANGES ON SPACE SIMULATION FOR ZrO_2 - TEFLON TFE 30 PAINT, DRIED AT ROOM TEMPERATURE
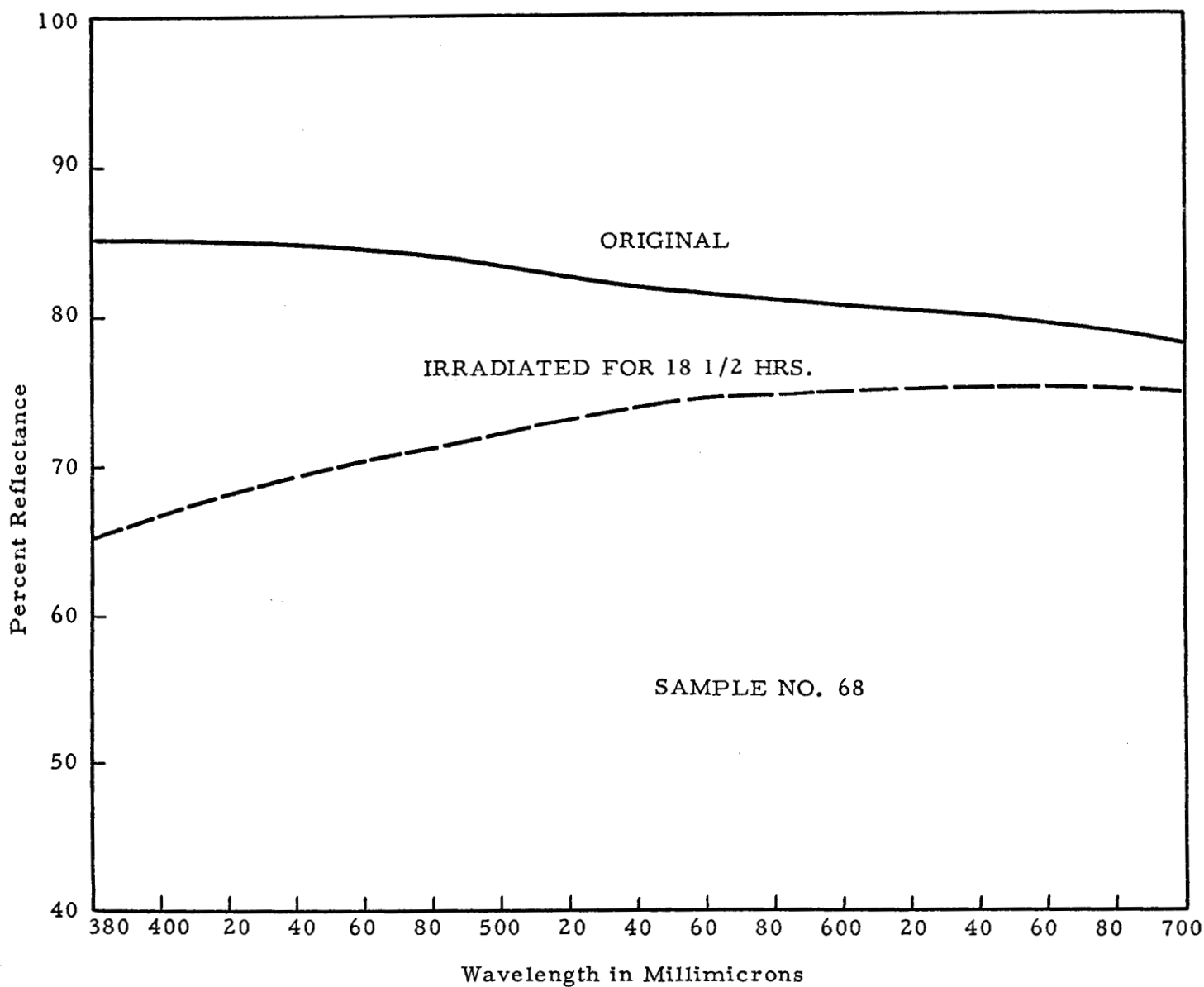
FIGURE 23 – REFLECTANCE CHANGES ON SPACE SIMULATION FOR
TEFLON TFE 30 PAINT VEHICLE, CURED FOR 16 HRS.
AT 320°F
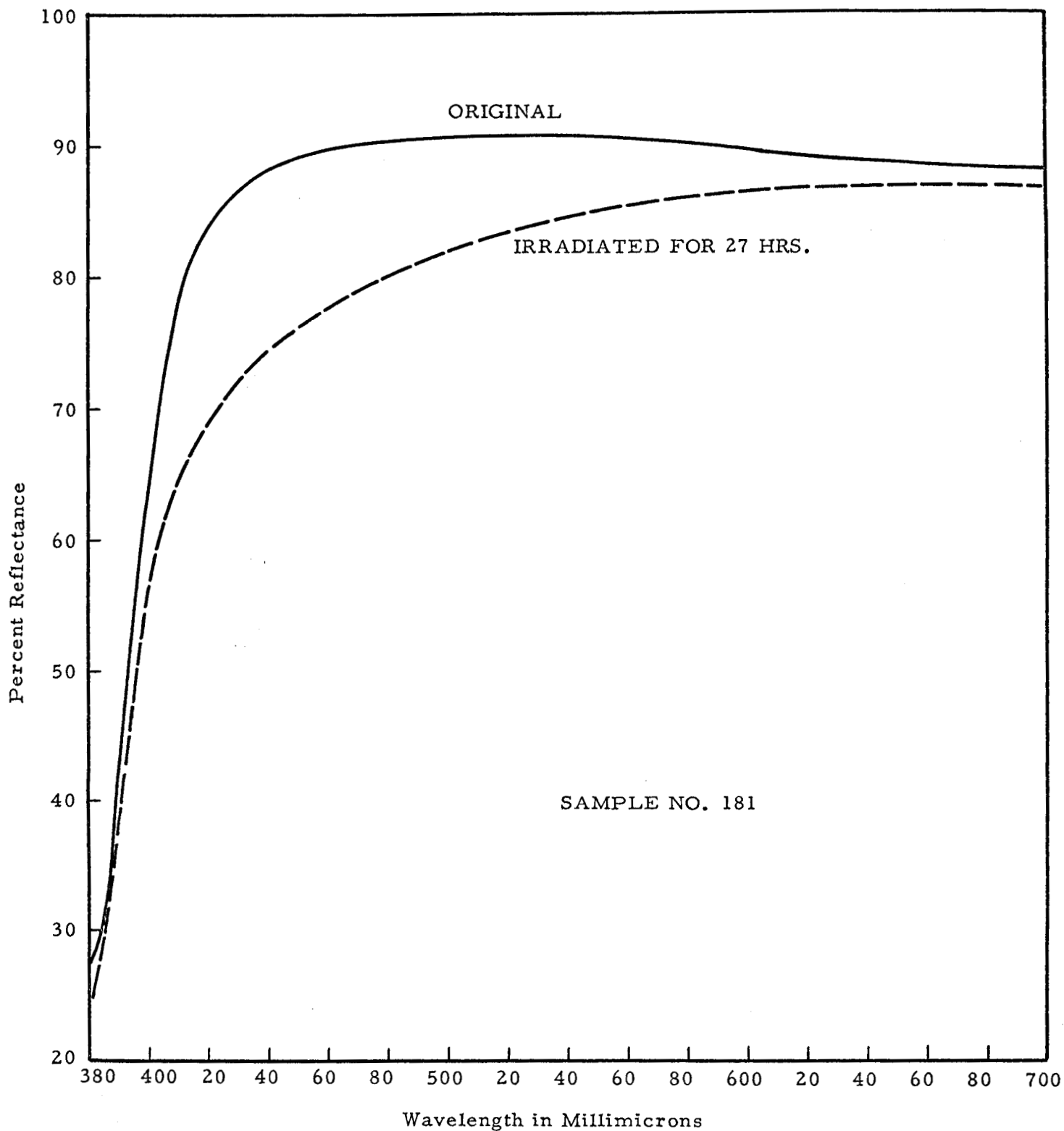
FIGURE 24 – REFLECTANCE CHANGES ON SPACE SIMULATION FOR ZnO-
VITON B PAINT, CURED FOR 24 HRS. AT 185°F AND FOR
24 HRS. AT 257°F
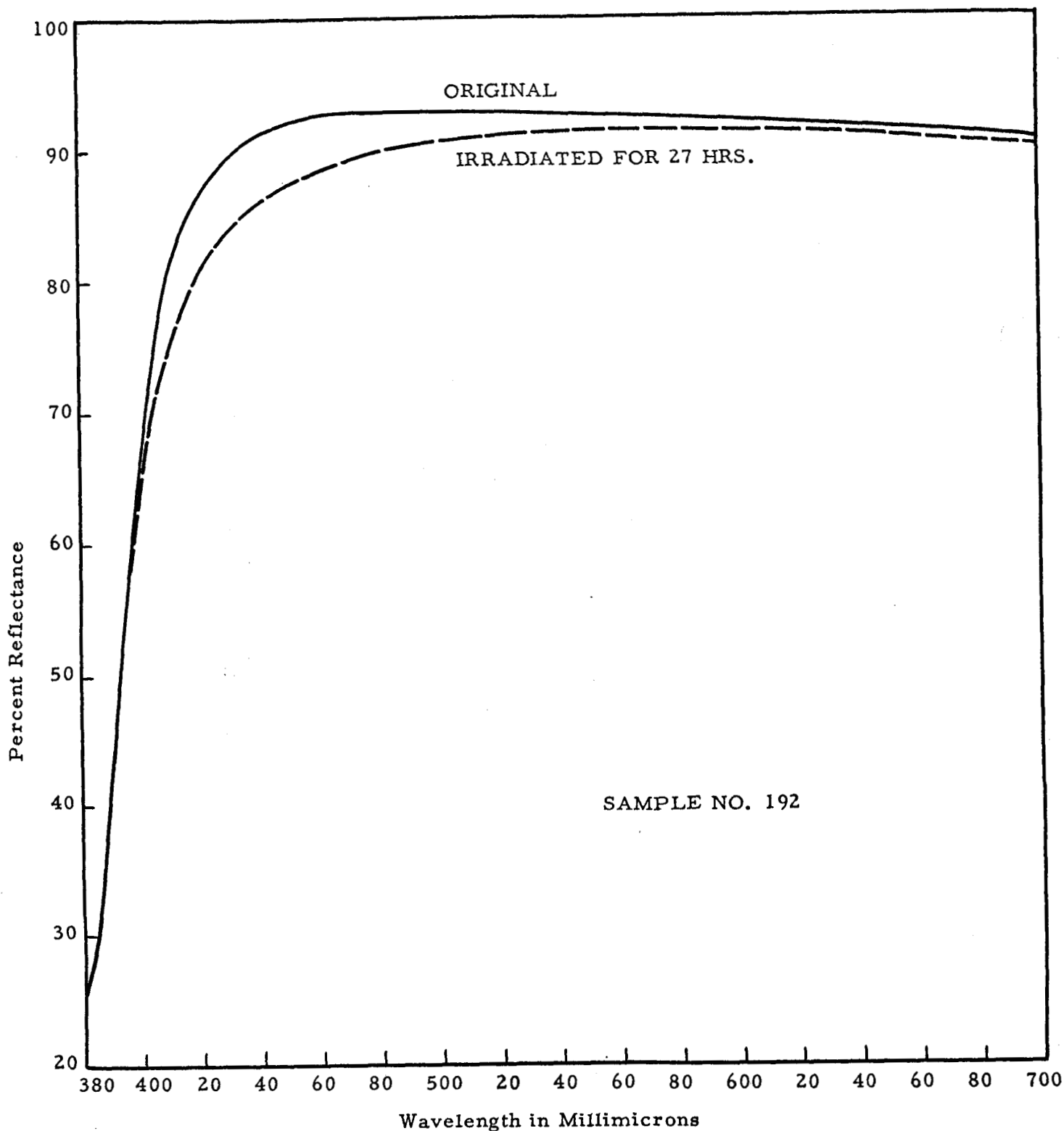
FIGURE 25 – REFLECTANCE CHANGES FOR ZnO-SILICONE RTV-11 PAINT,
CURED FOR 24 HRS. AT ROOM TEMPERATURE AND FOR 24
HRS. AT 300°F
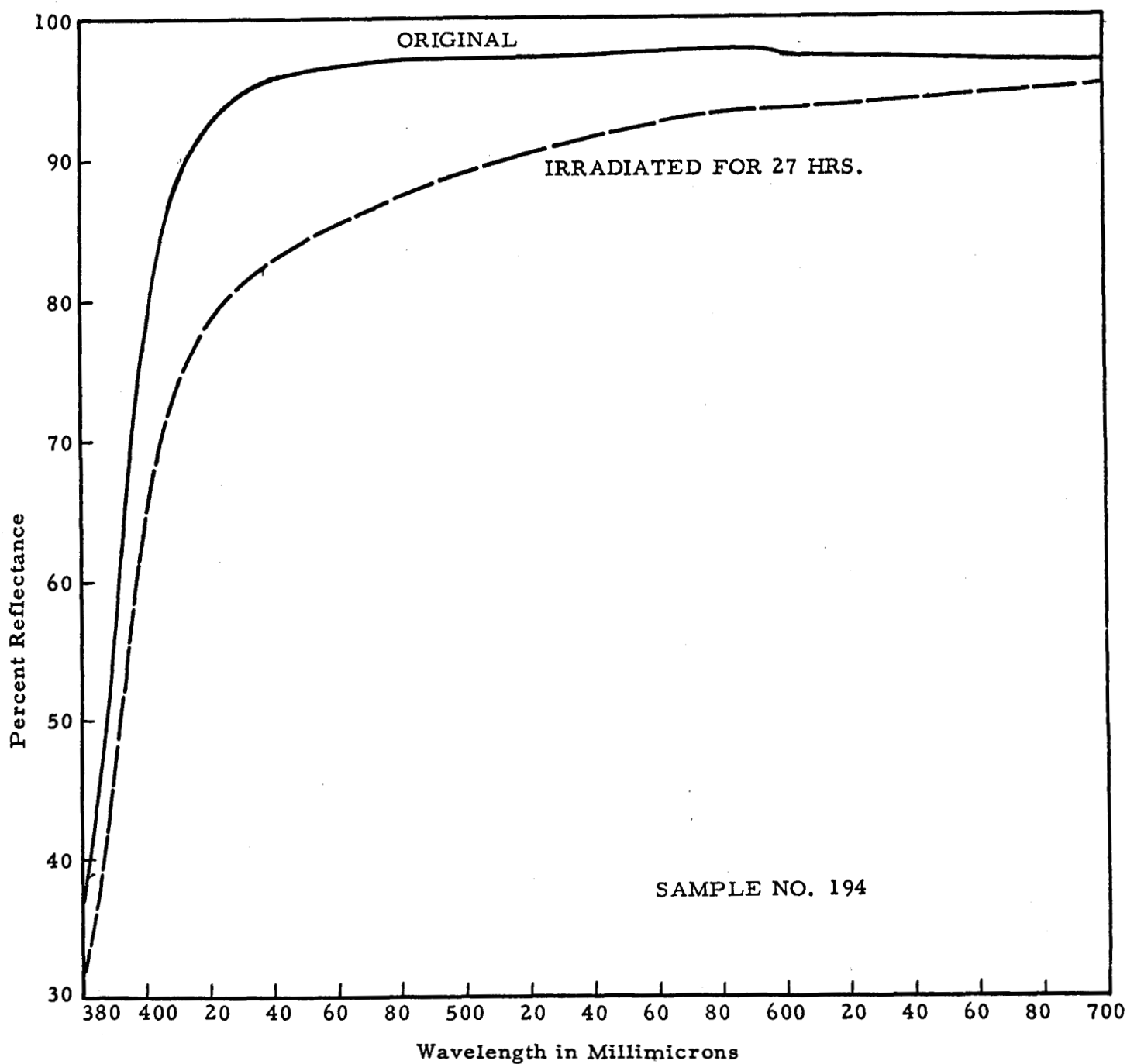
FIGURE 26 – REFLECTANCE CHANGES ON SOLAR SIMULATION FOR ZnO-
KEL-F 8213 (KETONE DISPERSION) PAINT, CURED FOR 24 HRS.
AT ROOM TEMPERATURE AND FOR 16 HRS. AT 300°F
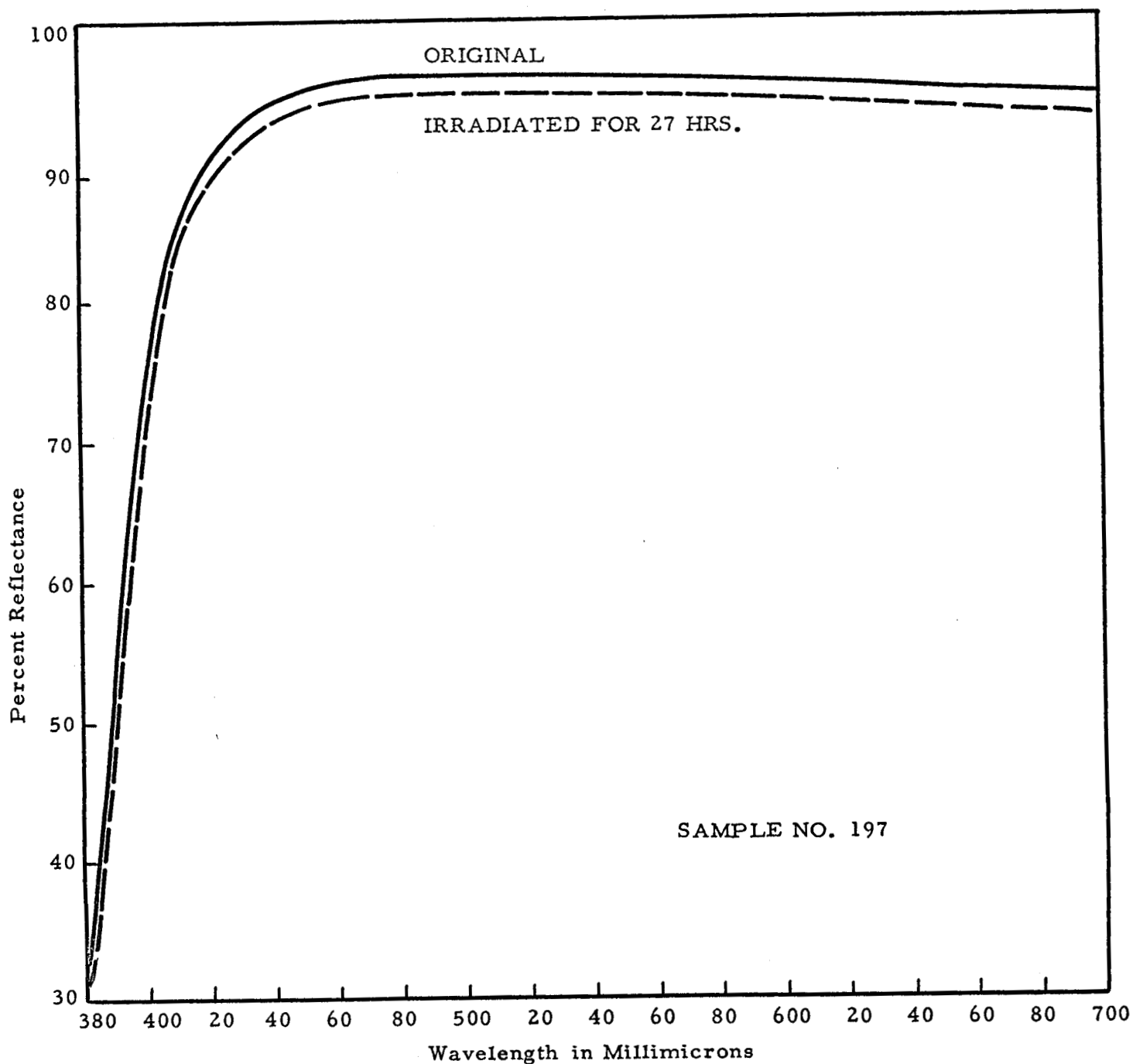
FIGURE 27 - REFLECTANCE CHANGES ON SOLAR SIMULATION FOR ZnO-
SILICONE LTV-602 PAINT, CURED FOR 16 HRS. AT ROOM
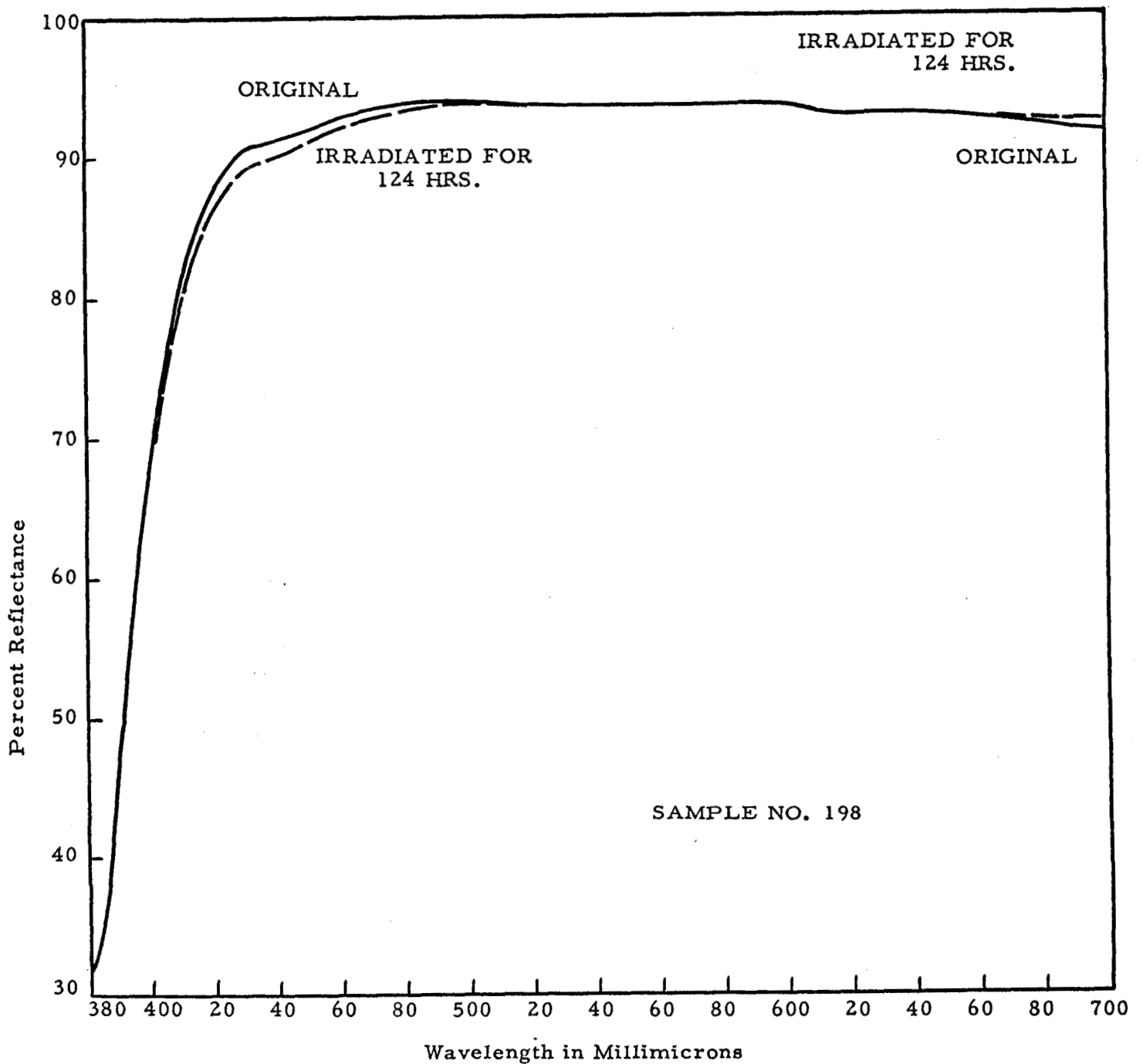TEMPERATURE, FOR 4 HRS. AT 248°F, AND FOR 4 HRS.
AT 302°F

FIGURE 28 - REFLECTANCE CHANGES ON SOLAR SIMULATION FOR ZnO-
SILICONE LTV-602 PAINT, CURED FOR 16 HRS. AT ROOM
TEMPERATURE, FOR 4 HRS. AT 248°F, AND FOR 4 HRS.
AT 302°F

VI.   DISCUSSION OF RESULTS

Modified Kel-Fs and Teflon did not show the UV stability expected. Kel-F 8213 (XVIII), Viton B, Kel-F clear solution (XXVII), other Viton modifications (XXIV, XXV, and XXVI) and Teflon 7 (IX) all were more or less unstable. Kel-F 8213 (XVII) and other modifications (XV and XX) may have some possibilities, but they are difficult to apply with ZnO or other pigments. Kel-F 800 (XVI), Exon 461 (XXIII) and Kynar L18 (XXII) discolored badly in UV.

RTV-11 Silicone Paste (IV) and LTV-602 Silicone Liquid (V) when pigmented with ZnO show considerable promise. Tests in progress during the writing of this report lasting for 124 hours at 6 suns show almost undetectable coloration. Silicones are discussed further under Future Work.

The results on inorganic materials and coatings have been discussed along with the tables and graphs. Further work is needed on the effect of water and calcining, particle size, and pigment purity before more detailed analysis. The outstanding UV stability of ZnO is particularly interesting and we have studied its properties further.

The Photolysis of Zinc Oxide

Photolysis and photoconductivity in a solid oxide are closely related. The raising of an electron from the highest filled band in a solid to the lowest conduction band is a partial breaking of a chemical bond, and any trapping of the electron, or of the hole left in the filled band, stabilizes the dissociated state. This trapping often involves surface states or surface reactions.

Zinc oxide has been studied extensively as a photoconductor[1] and catalyst[2,3] but we can merely summarize the most acceptable theory of its behavior here. It is normally an n-type conductor. When oxygen adsorbs on its surface a negative surface layer of oxygen ions forms and an electron depletion layer develops just below the surface. On the other hand, if the surface is reduced with hydrogen, or if zinc atoms are adsorbed, a conductive "enrichment" layer forms near the surface. An enrichment layer can be produced also by photolysis[4]. The light generates hole-electron pairs and the holes discharge surface lattice oxygen ions leaving excess zinc atoms. For the present discussion an important question is what is the effective vapor

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[1] E. Mollwo, Proceedings of the Conference on Photoconductivity, Atlantic City, Nov. 4-6, 1954, John Wiley and Sons, New York, 1956, p. 509.

[2] S. R. Morrison, Advances in Catalysis, Academic Press, New York, 1955, Vol. 7, p. 259.

[3] D. A. Melnick, Jour. Chem. Phys., 26, 1136 (1957).

[4] R. J. Collins and D. G. Thomas, Phys. Rev., 112, 388 (1958).

pressure of this excess zinc at about 300°K, and what effect does this excess zinc, or a doping agent such as lithium, have on further photolysis. As more and more holes are captured at the surface, a positive barrier builds up and limits diffusion of the holes to the surface. This same general reaction is well-known in AgBr, and the generation of metal by photolysis of CdS and ZnS has been reported.[5] In AgBr bromine is actually driven off by photolysis. In ZnO, adsorbed oxygen is first driven off, and then some lattice oxygen ions are neutralized by holes and driven off. If no zinc evaporates, the process will not go further because of the electric field opposing diffusion of holes to the surface. Of course, if a vehicle hinders the loss of oxygen or zinc the rate of the photolysis could be almost entirely determined by diffusion processes in the vehicle.

The effective vapor pressure of zinc over zinc oxide is not easily estimated because we are dealing with a solution of defects, including interstitial Zn^+, in electric and diffusion fields, but an estimate can be made on the basis of the observation that a zinc pressure from zinc metal at the same temperature as the zinc oxide produces the same semiconductor changes as photolysis by light.[4,6] Although zinc is one of the more volatile metals, its vapor pressure at 70°C corresponds to an evaporation rate[7] of only 0.1 micron/year. With a protective vehicle and a lower temperature (say 50°C) the rate should be much less. In other words, even if zinc does evaporate, the coating lifetime should be long enough to be useful.

If zinc oxide is exposed to an intense flash of light from a large xenon flashtube, sufficient reduced zinc is produced to give a test with phos-photungstic acid or other reagent sensitive to reducing agents. We have done this experiment with a 10,000 joule flash unit. We do not have proof that zinc metal is formed, but this is suspected because of the gray color which is produced by the flash, instead of the yellow color characteristic of interstitial Zn^+. Many of the pigments which have been exposed in our solar simulator give a similar gray color. Work is in progress on the exposure of single crystals of these pigment materials.

One problem in connection with coating stability is to determine what conditions of photolysis lead to segregation of metal in a crystal. In AgBr, metal segregates easily because of the high diffusion rate of Ag^+ and the strong metallic bond in silver metal. For oxides in contact with their respective metals, a fixed, low oxygen pressure and a temperature can be selected which will divide them into stable and unstable, but photolysis is not an equilibrium process. Whether or not metal segregates depends on the "solubility" of the metal in the oxide and the rate of generation of hole-electron pairs by the light. A further factor is the field structure which is built up

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[5] W. J. Merz, Helv. Phys. Acta, 30, 244 (1957).

[6] D. G. Thomas and J. J. Lander, Jour. Phys. Chem. Solids, 2, 318 (1957).

[7] L. D. Jaffe and J. B. Rittenhouse, JPL Technical Report No. 32-161, Evaporation Effects on Materials in Space.

by the light in a crystal. More light (of the "active" wavelengths) is absorbed near the surface of a crystal (or at the surface of a mass of pigment particles) and the ultimate steady state in the oxide will be determined by the intensity of this light at the surface and the oxygen pressure throughout the system. It is quite conceivable that excess metal could diffuse from the illuminated region to some other part of a crystal or coating where it would recombine with oxygen. Whether or not metal segregates in such a system depends on diffusion rates and the geometrical distribution of the light absorption and diffusion paths.

Moore and Williams[8] measured the solubility of zinc in ZnO and found that it could vary be a factor of ten according to the impurities present. A lot containing relatively high copper and silver contents dissolved more zinc. Their analyses for two lots, Lot A of which showed higher zinc solubility, were as follows:

p.p.m.	Cu	Ca	Fe	Na	Ag	Mg	Pb	Si
Lot A	10	2	1	1	1	0	0	0
Lot B	2	2	1	1	0	5	3	1

For Lot B a plot of log c against $1/T$ at 1 atmos Zn pressure gave a slope corresponding to $\Delta H° = 3.5$ kcal. At 1000°C the excess Zn was 0.009% at 1 atmos Zn pressure. In single crystals they found the diffusion rate of radioactive Zn^{65} to be given by $D_{Zn} = 1.3 \times 10^{-5} \exp(-43.5 \pm 11.0 \text{ kcal}/RT)$ $cm^2 sec^{-1}$ and the diffusion coefficient for oxygen to be $D_O = 6.5 \times 10^{11} \exp(-165 \pm \text{ kcal}/RT) cm^2 sec^{-1}$. The diffusion of the Zn was not dependent, at least in first order, on the pressure of Zn or O_2 over the crystals.

The solubility of Zn in ZnO has also been studied by Thomas[9], and if one extrapolates his high-temperature data to 330°K the solubility is found to be about 4×10^{10} atoms/cm^3. He found the heat of solution of a gaseous Zn atom in ZnO to be approximately zero, if it is assumed that all the zinc forms interstitial Zn^+. A concentration of 10^{10} atoms/cm^3 is extremely small for ZnO; supersaturated, metastable solutions are usually obtained by photolysis or quenching from elevated temperatures.

The effect of impurities has been studied mostly in connection with lithium, which introduces acceptor centers in ZnO. A crystal containing lithium takes up fewer negative oxygen ions per cm^2 in the dark than an undoped crystal, but light produces about the same quantity of excess zinc in the surface in both cases after a steady state is reached[4]. Copper and silver should behave like lithium, but monovalent impurities should oppose the dissolving of excess zinc, not aid it, as Moore and Williams appear to have found.

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[8]W. J. Moore and E. L. Williams, Discussions of the Faraday Society, No. 28, "Crystal Imperfections and the Chemical Reactivity of Solids," p. 86, 1959.

[9]Thomas, Jour. Phys. Chem. Solids, 9, 31 (1958).

The influence of water has been studied to some extent. When a photo-lysed ZnO crystal is exposed to dry oxygen the conductivity slowly diminishes toward the normal state due to oxidation of the excess zinc, but wet oxygen causes an almost instantaneous reduction of the electrical conductivity by a factor of at least 10,000. The mechanism of the action of water is far from clear, but it is evident from the literature that water and other impurities and defects at the surface of ZnO have a large effect on the stability.
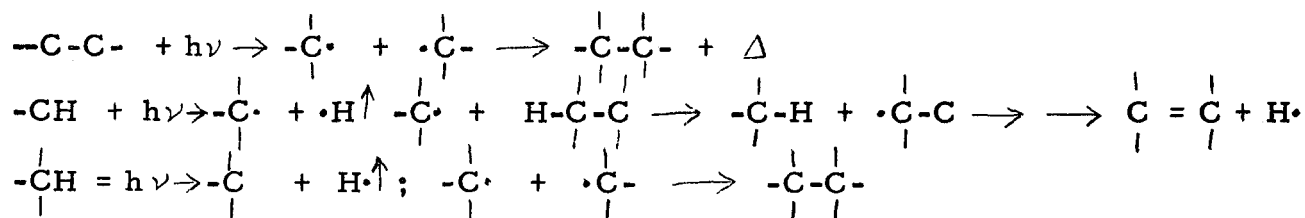
We do not like to conjecture much further without more experimental evidence, but there is some value in suggesting what to look for in the behavior of ZnO and ZnS. For the oxide applied as a pigment in a vehicle there may be an "induction" period during solar exposure over which photo-lysed oxygen slowly escapes through the vehicle until an enrichment, excess-zinc layer builds up in the surfaces of the ZnO particles. During this period the pigment will not discolor, but at some threshold time a relatively rapid darkening may occur because the oxygen held back in the coating is no longer at a high enough pressure to stop the segregation of free zinc. In the presence of light, this pressure is not the equilibrium thermodynamic pressure, but it is determined by several steady-state processes.

Zinc sulfide differs from the oxide in that sulfur is not as volatile as oxygen. G. Zerlaut (here at the Foundation) points out that phosphor-grade ZnS produces an odor of SO_2 when exposed to UV radiation in air. This may be due to the reaction of photolysed sulfur with adsorbed O_2-ions on the surface. Further photolysis may produce segregated sulfur which competes with the photolysis mechanism by reacting with free zinc generated by the light. This could account for the observation that ZnS coatings seemed to reach a steady state after a short exposure.
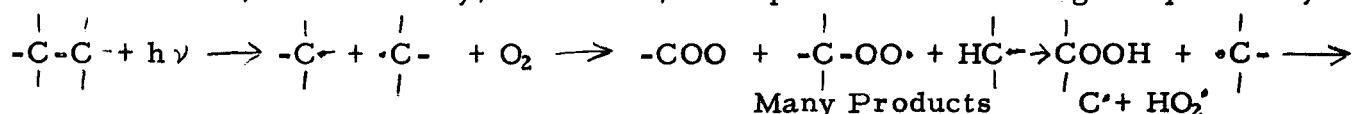
Although many problems remain, it is clear that a fairly self-consistent theory can be worked out and used as a guide for future work.

Competition Eetween Photooxidation and Photolysis in the Photodecomposition of Polymers

It has been shown clearly that the predominant reaction in the photoinduced decomposition of polymers in the presence of O_2 is oxidative, unless the polymer unzips to yield monomer. It has also been shown that the quantum yields in the absence of oxygen are much lower than they are when O_2 is present. The usual explanation for this is the so-called "cage effect". Although short wavelength ultraviolet light is sufficiently energetic to break carbon to carbon bonds, when these bonds are part of the backbone of the polymer, the radicals formed cannot diffuse away rapidly enough, as a general rule, to escape recombination. By contrast, when a carbon to hydrogen bond is broken, the hydrogen atom formed is highly mobile, and statistical probability of recombination is much reduced, and the eventual reaction is the production of a molecule of hydrogen, and the formation of a new crosslink or unsaturation, representing the recombination of two volatile fragments and two non-volatile fragments respectively. This does not preclude the existence of various chain transfer steps as intermediate reactions, but these do not contribute to the net reaction.

$$-C-C- + h\nu \rightarrow -\overset{|}{\underset{|}{C}}\cdot + \cdot\overset{|}{\underset{|}{C}}- \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- + \Delta$$

$$-CH + h\nu \rightarrow -\overset{|}{\underset{|}{C}}\cdot + \cdot H\uparrow \ -\overset{|}{\underset{|}{C}}\cdot + H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}} \longrightarrow -\overset{|}{\underset{|}{C}}-H + \cdot\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}} \longrightarrow \longrightarrow \overset{|}{C} = \overset{|}{C} + H\cdot$$

$$-\overset{|}{\underset{|}{C}}H = h\nu \rightarrow -\overset{|}{\underset{|}{C}} + H\cdot\uparrow ; \ -\overset{|}{\underset{|}{C}}\cdot + \cdot\overset{|}{\underset{|}{C}}- \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$$

It will be seen that the photolysis reaction is not a chain reaction. Compare this now to the photodecomposition of a molecule in the presence of O_2 which is a diradical in the ground state and hence a highly efficient scavenger of free radicals. Here the possibility of chain scission is much greater because of the essential irreversibility of the reaction with O_2. Moreover, this is a chain reaction, and this may, therefore, be expected to have a higher quantum yield.

$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- + h\nu \longrightarrow -\overset{|}{\underset{|}{C}}\cdot + \cdot\overset{|}{\underset{|}{C}}- \ + O_2 \longrightarrow -COO + -\overset{|}{\underset{|}{C}}-OO\cdot + H\overset{|}{\underset{|}{C}} \rightarrow COOH + \cdot\overset{|}{\underset{|}{C}}- \longrightarrow$$

$$\text{Many Products} \quad \overset{|}{C}\cdot + HO_2\cdot$$

The necessity to exclude oxygen rigorously, or, to consider the problem in another light, the influence of a small supply of oxygen, upon the two essentially competing reactions can be illustrated by considering the amount of O_2 required to react quantitatively with the photochemically generated radicals at energy levels which might be expected in the space environment.

Assume a solar intensity of 13 mwatts/cm^2 in the wavelength range between 2000 and 4000 A. Assume 75% of this energy is absorbed, and that all of the absorbed radiation is effective in breaking bonds. Since about 60 kcal/mole is required to break c-c bonds (and form 2 moles of C· radicals), we may calculate an upper limit of radicals formed as

$$10 \text{ mwatts/cm}^2 = 2.5 \times 10^{-3} \text{ cal/cm}^2 \text{ sec}$$

$$\frac{6 \times 10^4}{1.2 \times 10^{24}} = \frac{2.5 \times 10^{-3}}{X}$$

$$X = 5 \times 10^{16} \text{ radicals/cm}^2 \text{ sec}$$

In order to produce a similar number of collisions of O_2 with such a surface, the O_2 pressure would be approximately 2×10^{-4} mmHg, according to the following calculation.

The number of collisions/cm^2 sec $= \dfrac{nu}{\sqrt{6\pi}}$

where n = no. of molecules/ml

and u = root-mean-square velocity = $\sqrt{3RT/M}$

Therefore, $5 \times 10^{16} = 0.230 \text{ n} \sqrt{\dfrac{(3)(8.3 \times 10^7)(300)}{32}}$

$$n = 4 \times 10^{12} \text{ molecules/ml}$$

which corresponds to an O_2 pressure of

$$P = \frac{(4 \times 10^{15}) \, (0.082) \, (300)}{6 \times 10^{23}}$$

$$P = 2 \times 10^{-7} \text{ atm } O_2 = 2 \times 10^{-4} \text{ mm Hg, pressure of } O_2$$

It might be predicted that the reaction with O_2 will be appreciable at total pressures above 10^{-3} mm total pressure, at these radiation levels. At higher intensities, the O_2 requirements will be proportionally greater. In our equipment, the intensity is about five times greater, and the pressure is about three orders of magnitude less, so the probability of oxygen scission is negligible, if the O_2 were supplied from the atmosphere. The retention of whiteness observed with ZnO pigmented systems might be caused by a self-cleaning effect, similar to the chalking of anatase-pigmented house paints, since ZnO is known to be photochemically reactive, and since some organic vehicles are known to be photobleached in air after initial yellowing under vacuum irradiation. Without knowing or at least postulating the mechanism of such a reaction in some detail, it is difficult to estimate the consumption of ZnO required for such a mechanism, but if one makes a rough rule of thumb that one atom of oxygen would be required for each free radical produced, approximately one mole of ZnO would be required per cm^2/month of solar exposure - an absurd result. But if one assumes a quantum yield of 10^{-4}, a value often reported for oxidative photoinduced chain scission, this value drops to about 9 mg./month at the intensity of 13 mwatts/cm^2.

VII. FUTURE WORK

A. Inorganic Coatings

The outstanding performer in space simulation tests has been the zinc oxide-potassium silicate paint, and increasing emphasis will be placed on this composition. Maximization of the physical properties will be investigated. It is possible that a larger ZnO particle size than that of SP 500 (.25-.35 microns) may decrease the liquid requirements and lead to a tougher paint. Although the coarser materials available commercially are of lower purity and higher solar absorptivity, good solar stability may be retained by these powders. Various paints pigmented with the different grades of zinc oxide will be subjected to mechanical and optical measurements.

The area of composite coatings will receive closer scrutiny with emphasis on silicate-bonded ZnO on organic primers. The use of aluminum phosphate binder with ZnO is precluded by chemical reaction between the two during formulation.

The search for other possible pigments will be continued on a smaller scale. The diversity of particle sizes, shapes, and distribution afforded by some of the materials other than ZnO may present valuable information applicable to the ZnO-silicate studies.

B. Ultraviolet Resistant Polymers

Two ideal courses of action for the development of solarization resistant polymers are immediately apparent. They are the use and/or synthesis of polymers which are totally transparent to ultraviolet down to 2000 Å (the black body solar cut-off), or the use and/or synthesis of polymers with bond energies sufficiently great to resist cleavage even though ultraviolet is strongly absorbed. Since the first route is essentially impossible (e.g. certain acrylics, which absorb only at the shorter wavelengths, are thought to catastrophically un-zip), and since polymers with high bond strengths and thermal stabilities (e.g. many experimental organo-metallic and inorganic polymers) are usually highly colored, a compromise appears necessary. Such a compromise might consist of (1) the synthesis of a stable polymer backbone with essentially transparent ligands, or (2) the synthesis of polymers which do not show strong absorption and whose photodegradation processes do not involve the creation of highly colored species.

Therefore, it is not surprising that silicones have proved to be among the most solarization resistant polymers when irradiated in vacuum. The -Si-O-Si-O- backbone is both relatively transparent to ultraviolet and possesses high bond-strengths making main chain cleavage quite unlikely. Even more significant is the fact that phenylated — therefore ultraviolet absorbant — silicones are more highly discolored than methylated silicones. Short alkyl groups (e.g. methyl) are inherently more transparent to the longer wavelength solar ultraviolet. An example of polymers which may fit into the second category above are urea- and melamine-formaldehyde resins. They have shown sufficient resistance to discoloration, or yellowing, to warrant further investigation.

In accordance with the forgoing discussion, two lines of approach will be investigated. They are (1) the utilization of the inherently stable silicon-oxygen-silicon-oxygen backbone (or, $\left[\text{-M-O-M-O-}\right]_n$ when feasible) with primary emphasis on transparent and/or stable ligands and cross-linking groups, and (2) the investigation of urea-formaldehyde, modified urea-formaldehyde and other amino type resins.

Polymethyl(methoxy)siloxane polymers have been ordered and will be evaluated within the scope of this program. The procurement of reactive silicone pre-polymers and organo-silicon intermediates is contemplated for the purpose of preparing model compounds and polymers. Studies will be initiated in order to make certain of the more promising methyl silicones air-drying/curing.

Pure amine-formaldehyde resins have been ordered. Attempts to prepare stable amino-type resins based upon aliphatic diisocyanates will be initiated by the preliminary investigation of model compounds.

Paints

Paints will be prepared from the most promising resins which result from the investigations outlined above. It is planned to prepare both zinc

oxide and zinc sulfide pigmented coatings when possible. While the importance of evaluating the photochemical stabilities of the white pigments and pigment-binder combinations is recognized, studies of this nature are not contemplated within the immediate future. Primary-emphasis will be placed upon the procurement of a more satisfactory vehicle.

Primers for Ceramic Top-Coats

The use of organic primer coatings for the potassium silicate based inorganic paints has been discussed previously. The fact that the inorganic paints are relatively porous and that the most satisfactory means of their cleaning will likely involve the use of aqueous detergents makes the use of corrosion resistant primers necessary — particularly for light-alloy substrates. In addition to providing corrosion protection to the substrate, the organic primer layer should be chosen so as to provide for more conven-ient removal of the topcoat in the event of damage or thermal design changes. Still another advantage is the possibility of enhancing the emittance properties of the topcoat.

The curing temperature of 300°F for the topcoat and the fact that the primer must easily be wet by the aqueous inorganic paint solution poses limitations in the choice of primer vehicle. For example, silicones, which are hydrophobic, are precluded from consideration — as are all other notably hydrophobic resins. Investigations of suitable primer coatings will be initiated in the near future.

VIII. SUMMARY

Exposure of white pigments, organic and inorganic vehicles and pigmented coatings to simulated space solar radiation shows that ZnO and ZnS are unusually stable pigments, and that pure potassium silicate and special silicones are among the more stable vehicles. Calcined kaolin is less effected by UV than the uncalcined material, and other tests indicate that water is an important factor in radiation stability. Our results for ZnO and preliminary analyses of photolysis mechanisms in oxides and organic vehicles indicate that coatings of much improved stability can be developed.

Improved techniques of simulating and monitoring space solar radiation have been and are being developed. A special wide-view thermopile is being prepared for us by Eppley Laboratories, and improved traps on the space chamber have reduced varnish deposition on the mercury lamps.

Further work on ZnO, ZnS, potassium silicate, and silicone vehicles is projected. Pigments of larger particle sizes are being tried, and photolysis mechanisms in oxides are being analysed in more detail.

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